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UNITED STATES
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BUREAU OF MINES
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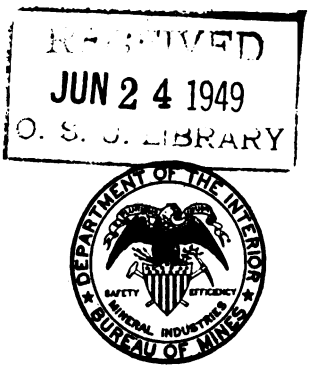
INFORMATION CIRCULAR

REPORT OF PETROLEUM AND NATURAL-GAS DIVISION

FISCAL YEAR 1946



BY

R. A. CATTELL AND OTHERS

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A Century of Conservation

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

REPORT OF PETROLEUM AND NATURAL-GAS DIVISION, FISCAL YEAR 1946[1]/

By R. A. Cattell[2]/ and Others

CONTENTS

	Page
Introduction	3
Acknowledgments	5
Helium production	6
Helium utilization and research	8
Process development	8
Helium survey	9
Helium tracer studies	9
Helium in welding and metallurgy	10
Transportation of natural gas	10
Natural gas hydrates	11
Removal of nitrogen from natural gas	11
Oil and gas development and production	12
Characteristics of gas-condensate fluids	12
Gas-condensate well corrosion	14
Petroleum engineering field studies	16
Carthage field	16
Lake Creek field	16
Sheridan gas-condensate field	17
New Hope field	17
Rangely field	18
Special study of Naval Petroleum Reserve No. 1, Elk Hills field, Calif.	18
Well-spacing studies	19
Studies of water-base and oil-base drilling fluids and water contents of formation cores	19
Correlations of physical properties of oil	20
Review of gas-conservation practices	21
Secondary recovery	22
Methods of increasing the recovery of oil	23
Field studies	23

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from the Bureau of Mines Information Circular 7506."

2/ Chief, Petroleum and Natural Gas Division, Bureau of Mines, Washington, D. C.

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	Page
Petroleum engineering studies in the Applachian region	25
Oil recovery from "black sands"	26
Laboratory research on reservoir drainage	27
Recovery of oil from outcropping bituminous sandstones by hot-water washing	27
Recovery of wax from crude petroleum wastes	27
Core and water laboratory	28
Recent trends in research	29
Petroleum chemistry and refining	30
Experimental sample processing	30
Continuous distillation	30
Superfractionation studies	31
Batch distillation of crude oils and their products.	32
Silica gel adsorption of naphthas and fuel oils	33
Desulfurization of naphthas, fuel oils, and crude oils	33
Hydrocarbon properties and analyses	35
Synthesis and purification of hydrocarbons	35
Properties of hydrocarbons	35
Development of spectrometric analytical methods	36
Development of non-optical analytical methods	37
Application of analytical methods to naphthas, fuel oils, and crude oils	38
Sulfur in petroleum	39
Synthesis of pure sulfur compounds	39
Fuel combustion in engines	40
Fuel response in spark-ignition engines (aviation and motor)	41
Aviation fuels, lean-mixture test	41
Aviation fuels, supercharge test	41
Motor fuels	42
Cooperative work	42
Fuel response (Diesel) in compression-ignition engines	43
Relationships of engine response, fuel composition, and fuel properties (physical and chemical)	43
General laboratory	46
Routine examination of crude oils	46
Standard inspection tests of petroleum products	47
Cooperative work	47
Miscellaneous	48
National Motor-Gasoline Semiannual Survey	48
Asphalts from Wyoming black oils	49
Utilization of natural gas for chemical products	49
Thermodynamics of petroleum	49
Heats of combustion	50
Flow calorimetry	51
Low temperature calorimentry	51

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ILLUSTRATIONS

Fig.		Following page
1.	Annual and cumulative production of Helium	6
2.	Windowed cell and auxiliary equipment	14
3.	Inhibitor injecting equipment, Cotton Valley, La., field	14
4.	Operator dropping sodium chromate sticks into well from loading magazine	16
5.	Composite curve of oil production showing effect of gas injection on 568 productive acres, Delaware-Childers field, Nowata County, Okla	24
6.	Pilot plant near ElDorado, Kans., for recovery of wax distillate from oil-field waste emulsions	28
7.	Bank of extraction units for determination of oil and water saturation of oil field cores	28
8.	Laboratory apparatus for study of selective plugging in oil sands	28
9.	Continuous distillation unit flow sheet	30
10.	Curves showing relationship of octane number to composition and distillation temperature	30
11.	Pilot-plant silica-gel adsorption column	32
12.	Silica-gel adsorption curves	32
13.	Typical absorption curves of samples containing benzene	32
14.	Diagram of apparatus for simultaneous determination of carbon and hydrogen	38
15.	Composition of fractions from typical crude oils	38
16.	ASTM-CFR fuel research unit for determining lean mixture knock characteristics of aviation fuels	40
17.	CFR supercharged fuel research unit for determining knock characteristics of aviation fuels	42
18.	ASTM-CFR fuel research unit for determining the knock characteristics of motor fuels	42
19.	Octane number of fractions containing methylcyclohexane in n-heptane	42
20.	Comparison of gasoline characteristics for summer surveys of 1936 through 1945	48
21.	Comparison of gasoline characteristics for winter surveys of 1935-36 through 1945-46	48
22.	Map showing locations and numbers of samples for the National motor-gasoline survey, winter 1945-1946	48
23.	Equipment for heats of combustion	50
24.	Heat-capacity laboratory	52

INTRODUCTION

With the surrender of the Japanese Imperial Government as a climax to the capitulation of the German High Command, the main objective of the Petroleum and Natural Gas Division pivoted from war assignments to its main normal functions. One of these functions is to give wide public distribution to valuable technical facts which the Division has obtained through research

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on petroleum, natural gas, helium, and related subjects. During the war years many engineering data and scientific facts could be released only on a restricted basis as reports to war agencies and others immediately concerned. Moreover, many of the wartime reports contained masses of detailed data that were prepared under stress to meet emergency schedules. For peacetime publication and application, these data must be reviewed, correlated, and rearranged so as to present the essentials in proper form. To illustrate, a wartime report of 50 pages might be resolved into one curve in a composite graph for a peacetime publication.

Another factor affecting the orientation of the work of the Division is the broader horizon of research revealed by its war activities. Fundamental research and careful engineering analyses are just as important in time of peace as in time of war; in fact, they should be more important to the forward view, because under peace conditions disrupting influences that distract from the orderly acquisition of knowledge are minimized.

Therefore, the concerted effort has been not to "salvage" the results of the war activities, but to evaluate them on the basis of their relative importance in the future economy of the country. Where wartime investigations have pointed to peacetime accomplishments, the effort has been to give the corresponding type of work additional emphasis. This adjustment can not be made hurriedly, but many of the necessary preliminary steps on the new course have been taken.

The general outline for treating the various activities and accomplishments of the Petroleum and Natural Gas Division has six main headings:

1. Helium production.
2. Helium utilization and research.
3. Oil and gas development and production.
4. Secondary recovery.
5. Petroleum chemistry and refining.
6. Thermodynamics of hydrocarbons.

Before discussing the individual problems in the six groups, a brief statement of the facilities for doing the work is offered to assist the reader in understanding the relations existing between the many projects worked upon by the Division. The Petroleum and Natural Gas Division is esentially a field organization and maintains only a very small headquarters staff in Washington, D. C. The activities are divided into two subdivisions, namely, (1) helium production and research and (2) petroleum and natural gas research.

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The helium activities in the field are centered at the Amarillo Helium Plant, which, in addition to producing helium, serves as an administrative headquarters for all helium plants and provides research facilities for helium problems and natural-gas problems closely associated with helium-plant operations. The administrative office directs the operations of the other helium plants at Exell, Tex., Otis and Cunningham, Kans., and Shiprock, N. Mex.

Petroleum and natural gas research is conducted at two experimental stations and three field offices. The larger petroleum experiment station is at Bartlesville, Okla. Four technical sections at this station conduct research on (1) development and primary production of oil and gas, (2) secondary recovery and special problems, (3) petroleum chemistry and refining, and (4) thermodynamics of hydrocarbons. Special emphasis is placed on problems of the Mid-Continent, but consideration is also given to research of a broad national scope. The second station is the Petroleum and Oil Shale Experiment Station, Laramie, Wyo. Besides studies on oil shale and shale oil, research on petroleum production, chemistry and refining are conducted with special emphasis on problems of interest to the Rocky Mountain region. Part of the basic research on sulfur compounds in petroleum is carried on at Laramie.

The Petroleum Field Office, Franklin, Pa., conducts production research in the Appalachian region, with special attention to secondary recovery. At Dallas, Tex. another Petroleum Field Office makes engineering studies of oil and gas fields in Texas, Louisiana, Arkansas, and New Mexico, the Bartlesville Station assisting with laboratory and special field facilities. The third and oldest field office and laboratory of the Division is at San Francisco, Calif., and conducts research on drilling muds, production problems, and the recovery of bitumens from "tar sands."

ACKNOWLEDGMENTS

Nearly all of the scientists and engineers of the Division have made important contributions to the preparation of this report. These were correlated at the field headquarters, which have the following supervising engineers:

C. W. Seibel, Bureau of Mines Helium Plants, Amarillo, Tex.

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S. S. Taylor, Petroleum Field Office, Franklin, Pa.

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Special acknowledgment is made to H. C. Fowler, who placed much of the material in proper form for publication, and N. A. C. Smith for constructive review of the text.

HELIUM PRODUCTION

The principal naval and military use of helium during the war was for the inflation of blimps and barrage balloons. Blimps were used very extensively for coast patrol and convoy duty outside of the immediate combat areas. Their success in this service is summed up in the statement.3/

"In all, blimps escorted 89,000 surface craft in World War II without a single loss to enemy submarines. Of these, 50,000 were in areas where U-boats were known to be present at the time.* * *. After Airship Squadron 14 began operations in the Gibraltar area in June 1944, not a single enemy submarine passed through the strait, either by day or night." Helium-filled balloons assisted in obtaining highly important data for forecasting weather - a vital service to civilian and military operations. Helium also was used in welding magnesium, aluminum, and other metals into critical war materials.

Prior to December 7, 1941, the Bureau of Mines had only one helium-production plant - at Amarillo, Tex. An expansion program was started, during which the rated capacity of the Amarillo plant was increased 50 percent, and plants were built at Exell, Tex., Otis and Cunningham, Kans., and Shiprock, N. Mex., in rapid succession, to increase the capacity for production from a prewar rate of 2 million cubic feet to a wartime capacity of 20 million cubic feet per month. Actually, the production capacity was found to be 27 million cubic feet per month. The designed capacity and the proved capacity under peak operations for each of the plants are given in table 1:

TABLE 1. - Helium production capacity, million cubic feet per month.

Plant	Designed	Demonstrated
Amarillo	3	4
Exell	5	7.5
Otis	4	5.
Cunningham	4	4.5
Navajo	4	6
	20	27

The schedule of building the plants and producing helium from each after completion was coordinated with naval and military needs. At no time during the war emergency was the Bureau of Mines unable to furnish promptly all the helium requested of it by the armed services, all other Governmental agencies, and commercial users. The total volume of helium produced at each of the Bureau's helium plants, by fiscal years since 1940, is shown in table 2.

3/ Rosendahl, C. E., Rear Admiral, U. S. Navy: "They Were Dependable."

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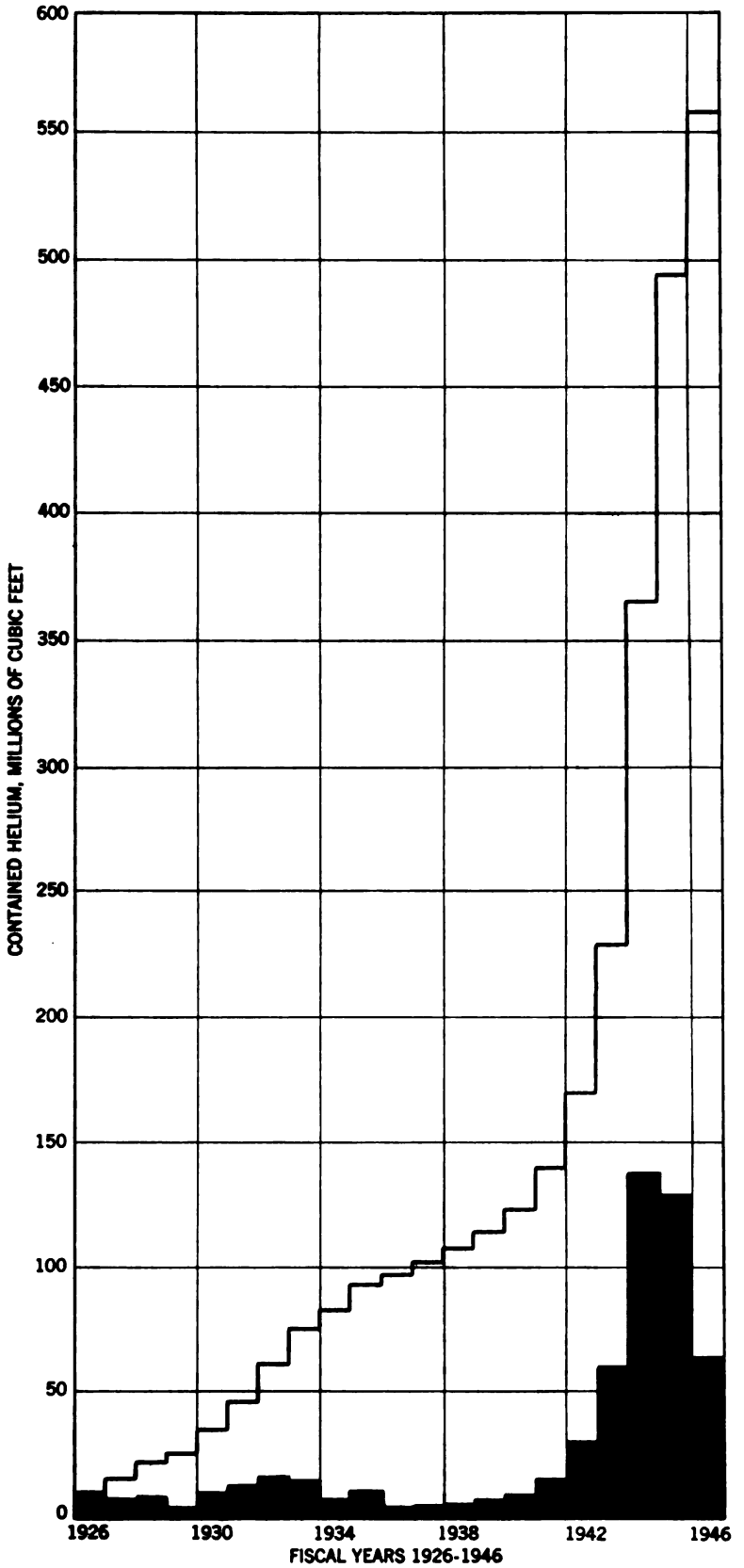

Figure 1. - Annual and cumulative production of helium by the Bureau of Mines helium plants.

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TABLE 2. - Total helium produced at each plant, by fiscal years, during the period July 1, 1940, to June 30, 1946.

Plant	1940	1941	1942	1943
Amarillo	9,450,855	16,173,430	29,962,530	40,997,490
Exell				17,953,670
Otis				
Cunningham ..				
Navajo				
Total ..	9,450,855	16,173,430	29,962,530	58,951,160

Plant	1944	1945	1946
Amarillo	34,436,360	17,740,604	5,414,910
Exell	62,448,050	52,067,850	55,078,455
Otis	25,198,520	28,942,455	2,492,780
Cunningham	12,941,800	29,690,000	417,200
Navajo	2,243,414	-	-
Total	137,268,144	128,440,909	63,403,345

Large-scale production of helium was started under the supervision of the Navy Department during World War I and remained under that Department until the end of fiscal year 1925. During that time a total volume of 23,994,488 cubic feet of helium was produced. The maximum volume of helium in any one year during this period was in 1925, when 9,418,363 cubic feet was produced. Helium production was transferred to the Bureau of Mines on July 1, 1925. The yearly and cumulative production of helium on a fiscal-year basis since that time is shown in fig. 1.

The war demands for helium reached a peak during 1944 and declined somewhat in 1945. Fortunately, enemy-submarine activities diminished, and the demand for helium by the armed services decreased further. This resulted in shutting down the Navajo Helium Plant in March, 1945. VE and VJ Days eliminated the war use of helium, and the Cunningham and Otis plants, in succession, were shut down. The Navajo and Otis plants were placed in stand-by status, so that they may be started up again on relatively short notice. Decision was made to dismantle the Cunningham plant, however, as the supply of helium-bearing natural gas available to it was almost depleted and would be progressively depleted by withdrawals to supply commercial fuel-gas markets.

The number of employees engaged in the production of helium was reduced by 60 percent during the fiscal year. During this same period the volume of produced helium was reduced by only 51 percent. Thus, more helium was produced per employee this fiscal year than last, though a small force of employees was left at the Otis and Navajo plants to maintain them in good condition.

Commercial sales of helium have increased consistently during the past several years. Sales during the last month of this year were over twice as high as in any previous month and 7-1/2 times as high as in the month following VJ day. Commercial sales during the year totaled 4.2 million cubic feet.

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During the war Army-Navy "E" awards were presented to three of the Bureau's helium-production plants, and two of these plants won the "E" for the second time. Auxiliary Military Police awards of Merit were presented by the Army to the auxiliary military police forces of two of the plants. Awards of excellence were presented to two of the Bureau's staff by the Secretary of the Interior for work relating to helium, and Awards for Heroism were awarded two of the staff of one of the helium plants by the Joseph A. Holmes Safety Association.

Conservation of helium that otherwise would go to market with the natural gas, if not extracted by the Exell Helium Plant, was continued during the year by storing it underground in the Cliffside Gas Field. A total volume of 28,930,020 cubic feet was delivered to underground storage during this fiscal year, which, added to the 20,629,400 cubic feet so stored in the fiscal year 1945, makes a total cumulative volume of 49,559,420 cubic feet of conservation helium now in underground storage.

HELIUM UTILIZATION AND RESEARCH

The process and equipment used in the helium production plants to extract helium from natural gas were developed by Bureau research. During this fiscal year an expanded program of helium research was initiated to improve the efficiency of extraction and the purity of helium produced, to maintain adequate reserves of helium-bearing natural gas, and to develop and make available to industry and the general public new uses for helium. Helium is a natural resource available in quantity only in the United States, and it is the Bureau's sincere desire to supply ample quantities to Governmental agencies, industries, and the public. At the present time, all commercial demands as well as all Government requirements are being met by extracting only a part of the available helium that otherwise will be lost through pipelines supplying commercial fuel markets.

Process Development

The helium normally produced in the Bureau of Mines plants is about 98.2 percent pure, the impurity being mostly nitrogen and a trace of hydrogen, which apparently is present originally in the natural gas. It has long been the desire to increase helium purity so as to increase the lift of balloons filled with it; for pure helium, though only 1.8 percent better than helium now being produced, may increase the pay-load-carrying capacity of a lighter-than-air ship by 10 to 15 percent. In addition, relatively recently developed commercial processes demand helium of greater than 98.2 percent purity. Equipment was built several years ago by the Bureau to permit producing relatively small volumes of essentially pure (99.8 percent, or better) helium by adsorption of the impurities on activated cocoanut charcoal maintained at liquid-nitrogen temperatures. This initial equipment was not suitable for continuous plant-scale production, however, and this year a research program was started to develop a modification of the charcoal-adsorption process suitable for continuous large-scale operation. A pilot unit was designed and constructed and was successful in increasing helium purity from the initial 98.2 to 99.8 percent, the impurity being largely hydrogen

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that was present originally in the natural gas from which the helium was extracted. Under some conditions, a large part of the hydrogen also apparently was adsorbed to give a helium of 99.9 plus percent purity.

Materials then were ordered to build pressure vessels holding activated carbon for installation on each purification unit at the Exell Helium Plant. When installed, purity of the standard-production helium will be raised from 98.2 to 99.8 percent or better. Work is still going on in an attempt to produce 100-percent helium. The ability to provide high-purity helium probably will result in additional uses being found for this gas in metallurgy, welding, and other industrial applications.

Helium Survey

The Bureau has ample reserves of helium-bearing natural gas to furnish all helium needs forseeable in the next decade or more. It realizes, however, that these reserves are not inexhaustible, and it is constantly on the alert to find new sources of the gas, which work is proceeding along four general lines:

1. Collection of gas samples from existing fields and new discoveries.

2. Analysis of gas samples for helium content and for other components and physical characteristics pertinent to helium extraction.

3. Engineering studies of the fields with high helium content to determine reserves of helium and producing characteristics of the fields.

4. Preparation of recommendations for acquisition of new reserves.

A new field having high helium-content natural gas was discovered early in the recent war. An engineering study was made with the result that a plant was built to extract the helium from the gas. Since the end of hostilities a decision has been made to prepare and publish a report[4/] giving the information obtained during the engineering studies of the field, and this report was about 95 percent completed at the end of the year.

A few samples of gas from wildcat wells in the United States were analyzed during the year. Gas-fractionating equipment and new combustion-analysis equipment were ordered.

Helium-Tracer Studies

During the war, the Bureau of Mines, at the request of the Navy Department, rendered engineering assistance in the development of the Naval Petroleum Reserve No. 1, Elk Hills, Calif. field, and in this connection conducted the first helium tracer gas project. When used as a tracer,

4/ Hinson, H. H., Reservoir Characteristics of Rattlesnake Oil and Gas Field, San Juan County, New Mexico: Bulletin of the American Association of Petroleum Geologists, Vol 31, No. 4, April 1947, pp. 731-771.

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helium is mixed in relatively small concentration with natural gas that is being injected into producing formations of oil and gas fields. The appearance of this helium in the gas produced at various producing wells surrounding the injection well reveals valuable information on the movement of the injected gas. The project was completed this year, and two reports 5/ 6/ were published.

A new helium tracer-gas project was started in December in the Slaughter field in West Texas, and in June of this fiscal year a program was started in the Cabin Creek field of West Virginia. The excellent results obtained in the Elk Hills field have created a great deal of interest among oil and gas companies, and approximately 80 inquiries were received relative to the helium-tracer work. Several companies have indicated a desire to start helium-tracer programs. Another indication of the importance of this tool to industry is the recent inquiry by a service company regarding a license to undertake helium-tracer work on a commercial basis.

Helium in Welding and Metallurgy

Early in the fiscal year, surveys were made to determine the present uses of helium in welding and metallurgy and to explore, with commercial concerns, the possibility for new uses for helium in these fields. It was quite evident from this survey that the use of helium in metallurgy and welding, especially the development of new uses, would depend on the ability to obtain helium of higher purity.

As a result of this inquiry, it was decided to conduct research on the use of helium in welding and metallurgy. Some work was completed on the welding of magnesium and stainless steel. Equipment was purchased to extend the research on the use of helium in metallurgy and welding.

TRANSPORTATION OF NATURAL GAS

The next two research problems deal with transportation studies that are closely related to the operation of the Bureau of Mines helium plants and are of great interest to companies engaged in transporting natural gas from gas fields to distant markets. The research is being conducted at the Amarillo Helium Plant and is being presented at this point to complete the discussion of the research program at Amarillo, rather than to follow the normal sequence of petroleum and natural-gas research and describe the work following the discussion of the oil and gas development and production studies.

5/ Frost, E. M., Jr., Helium Tracer Studies in the Elk Hills, California, Field: Bureau of Mines Rept. of Investigations 3897, 1946, 6 pp.

6/ Frost, E. M., Jr., Improved Apparatus and Procedure for the Determination of Helium in Natural Gas: Bureau of Mines Rept. of Investigations 3899, 1946, 16 pp.

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NATURAL-GAS HYDRATES

Prior to the entrance of the United States into World War II, the Bureau of Mines, in cooperation with the American Gas Association, was engaged in the study of natural-gas hydrates. These hydrates are solid, icelike compounds that may, and often do, form inside of natural gas pipelines during the cooler, though not necessarily freezing, seasons of the year. Under severe conditions, they often completely close even the largest pipelines and completely stop the flow of gas.

Because of assignments of personnel to essential war work, it was necessary to suspend the hydrate work from December 1941 to December 1945. Upon its resumption, the Bureau's previous research was reviewed, and it was found that the objective of the problem apparently had been attained. Some data had been collected that had not been published, and a paper[7] presenting these was written.

To close out the problem, a general review of the literature on gas hydrates was made, and a comprehensive report[8] on the subject then was begun in which the data obtained by the Bureau throughout the investigation would be incorporated and supplementary data of other investigators would be reviewed and summarized where appropriate.

REMOVAL OF NITROGEN FROM NATURAL GAS

Most of the known helium-bearing natural gases contain appreciable quantities of nitrogen, in some cases[9] more than 70 percent.

In the process of helium extraction, not only the helium but also a part of this nitrogen is removed from the gas. The removal of these noncombustible constituents increases the percentages of combustibles and results in a higher heating-value gas than was originally produced from the well.

This increase in heating value is of economic interest to the owners of natural-gas properties and to the operators of commercial natural-gas pipelines supplying fuel markets, especially if larger percentages of nitrogen than are being removed by the helium plants can be taken out by a suitable process. This will permit selling initially high-nitrogen gases that otherwise are unsalable because of low heating value. It also will increase

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7/ Frost, E. M., Jr., and Deaton, W. M., Gas Hydrate Composition and Equilibrium Data: Paper presented at meeting of Natural Gas Department, American Gas Association, Cincinnati, Ohio, May 1946.

8/ Deaton, W. M., and Frost, E. M., Jr. Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines: In preparation; to be published by the American Gas Association as a Bureau of Mines Monograph.

9/ See footnote 4.

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the capacity of pipelines to carry gas owing to the decrease in viscosity and density of the processed gas which accompanies the removal of nitrogen.

Experience gained by Bureau of Mines engineers in operating helium plants indicates that a combination liquefaction and fractionation process can be designed to separate most if not all of the nitrogen from the hydrocarbons of natural gas. However, the whole field should be explored thoroughly before a process or combination of processes is selected for further design and construction. Work to date by the Bureau of Mines on this problem comprises a preliminary survey of the literature, and study of proposed process cycles to effect separation of the nitrogen from the hydrocarbons.

Several companies in the natural-gas industry have evinced interest in this problem. The American Gas Association may enter into a cooperative agreement with the Bureau to accelerate the work.

OIL AND GAS DEVELOPMENT AND PRODUCTION

Production engineers of the Bureau of Mines carried out their special war assignments with the view of giving assistance, first, to the Petroleum Administration for War. Studies were conducted by physical chemists and engineers of the Bartlesville Station and the Dallas field office on 12 condensate-bearing fields selected because the extractable quantities and the characteristics of the components in them were believed to be suitable for the manufacture of aviation gasoline and other war-essential products. The production characteristics of the reservoirs were investigated, and detailed reports were made to the PAW and the operators especially concerned. Many of the data are being supplemented by additional experimentation so that reports may be prepared for publication.

Work was continued on other problems that had their inception as war assignments because information of permanent value to the petroleum industry could be obtained by their completion. For example, beginning in March 1945, engineers of the Bartlesville station and the San Francisco office collaborated with the U. S. Navy in determining reservoir performance in Naval Petroleum Reserve No. 1, Elk Hills, Calif. A report has been prepared for publication based upon the detailed progress reports submitted to Navy representatives and to the engineering committee of the Unit Operators. This first report describes concisely the results of the various phases of the subsurface engineering study in the Elk Hills field.

Characteristics of Gas-Condensate Fluids

Knowledge regarding the composition of gas-condensate fluid, especially the type and quantity of hydrocarbons available in particular reservoirs, is exceedingly important to the oil and gas industries of the country. Operators also need information concerning the amount and behavior of water vapor and other substances associated with the hydrocarbons in the reservoir. Some of the substances in the fluid from high-pressure gas-condensate wells cause serious internal corrosion of tubing and other well equipment, creating

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a distinct hazard to life and property. Therefore, an immediate part of the Bureau's work is a search for means to prevent this condition. In the study of both these problems (the major one deals with fluid composition and its subsidiary, ascertaining the nature of corrosion, and finding of inhibitors) the Bureau of Mines has received active cooperation from the Natural Gas Department of the American Gas Association and from the Natural Gasoline Association of America.

The studies of the characteristics of gas-condensate fluids, including corrosion research, resulted in the publication of five reports, some of which describe the development of new research equipment, whereas others present data developed from the use of this apparatus or of previously used equipment.

The first published report 10/ of the group describes the equipment and procedure used to determine the presence of water in different parts of the tubing of a producing well and gives the results obtained. The test equipment was used in measuring the liquid:gas ratio of water in the tubing of a flowing gas-condensate well in the Saxet field near Corpus Christi, Tex.; hydrocarbon liquid:gas ratio data also were determined in the temperature range 86° to 280° F. and over the pressure range 450 to 3,200 p.s.i.a. The liquid:gas ratio of the water was found to range from a trace at the bottom of the flowstring to 0.020 gallon per M cubic foot at the surface. The hydrocarbon liquid:gas ratio was zero in the reservoir as the dewpoint pressure of the fluid at reservoir temperature was less than the reservoir pressure. At the flow rate of the test, hydrocarbon liquid formed only after the fluid had moved more than 600 feet up the tubing. The liquid:gas ratio then increased until at the surface, at wellhead pressure and temperature, it was 0.76 gallon (or more) of hydrocarbon liquid per M cubic foot of gas.

Because water as well as corrosive substances must be present before corrosion can take place, this work on fluid characteristics has direct application to the study of well corrosion, discussed more specifically in the subsection which follows. The finding of liquid water throughout the full length of the tubing does not mean that corrosion necessarily will occur throughout, but it has been found that this condition is an important aid when treating a well to minimize corrosion.

Gas-condensate field production practices, consistent with a sound program of conservation, are guided in large measure by a knowledge of phase relations for each particular fluid, and both static and dynamic methods for determining these properties have been used by the natural-gas industry in recent years. Since 1936, the Bureau of Mines has been using static laboratory procedures for investigating the phase relations of gas-condensate fluids. By 1943, these studies had progressed to a point where a dynamic method

10/ Eilerts, C. K., Smith, R. V., and Barr, V. L., Measuring Distribution of Liquids in Flowstring of a Gas-Condensate Well: Oil and Gas Jour., Dec. 15, 1945, p. 91.

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involving portable equipment was developed. A method of wellhead sampling[11] of the flowing gas-condensate fluid was developed by the Bureau, as sampling is an extremely important part of the dynamic test procedure. The results of nine sampling tests are reported to provide information helpful in the routine sampling of wells not equipped with separators and stock tanks.

The most recent development of equipment for determining the relative volumes and compositions (at equilibrium) of the liquid and gas phases of fluid produced from gas-condensate wells was the windowed cell [12] shown in figure 2. This equipment was designed and built to obtain critical pressure and temperature data on hydrocarbon mixtures in ranges unattainable with the equilibrium cell and equipment in the portable laboratory, which has been widely described in the literature. Volumetric liquid:gas ratios below 70° F. cannot be determined with the portable equipment because of the difficulty of conducting tests involving the flow of fluids that contain hydrates. Laboratory and field testing indicated that the critical temperature could not be determined by dynamic methods unless the natural hydrocarbon mixtures contained more than 4 gallons of butanes and heavier components per M cubic foot. The windowed cell was designed to provide a static test procedure that would require no flow-control valves that might be stopped by solid hydrates. An especially designed system of windows permits safe observation and volume measurement of the coexisting liquid and gas phases of the hydrocarbon mixture in equilibrium.

Gas-Condensate Well Corrosion

The study of corrosion in gas-condensate wells is being conducted through experimentation in the laboratory and in the field along two main lines:

1. To ascertain the nature of the corrosion and to find inhibitors that will minimize the corrosive effects

2. To compare alloys and other substitutes with standard carbon steels (as to composition, fabrication, and resistance to corrosion) with the view of finding economically feasible materials that may be used with safety.

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[11] Eilerts, C. K., Smith, R. V., Carlson, H. A., Mooney, C. V., Harris, H. M., and Barr, V. L., Wellhead Sampling of Flowing Gas-Condensate Well: Presented before High-Pressure Gas Sampling Research Committee, Natural Gasoline Association of America, November 1945. Published in Proceedings of Natural Gasoline Association of America, 1945-46, Dec. 1946.

[12] Eilerts, C. K., Barr, V. L., Hamontre, H. C., Bobrowski, F., and Mullens, B. N., Windowed Cell for Observing Hydrocarbon Phases under Variable Pressures: Presented at the Convention of the Natural Gas Department, American Gas Association, Cincinnati, Ohio, May 7, 1946. To be published in the Proceedings of the American Gas Association, 1946.

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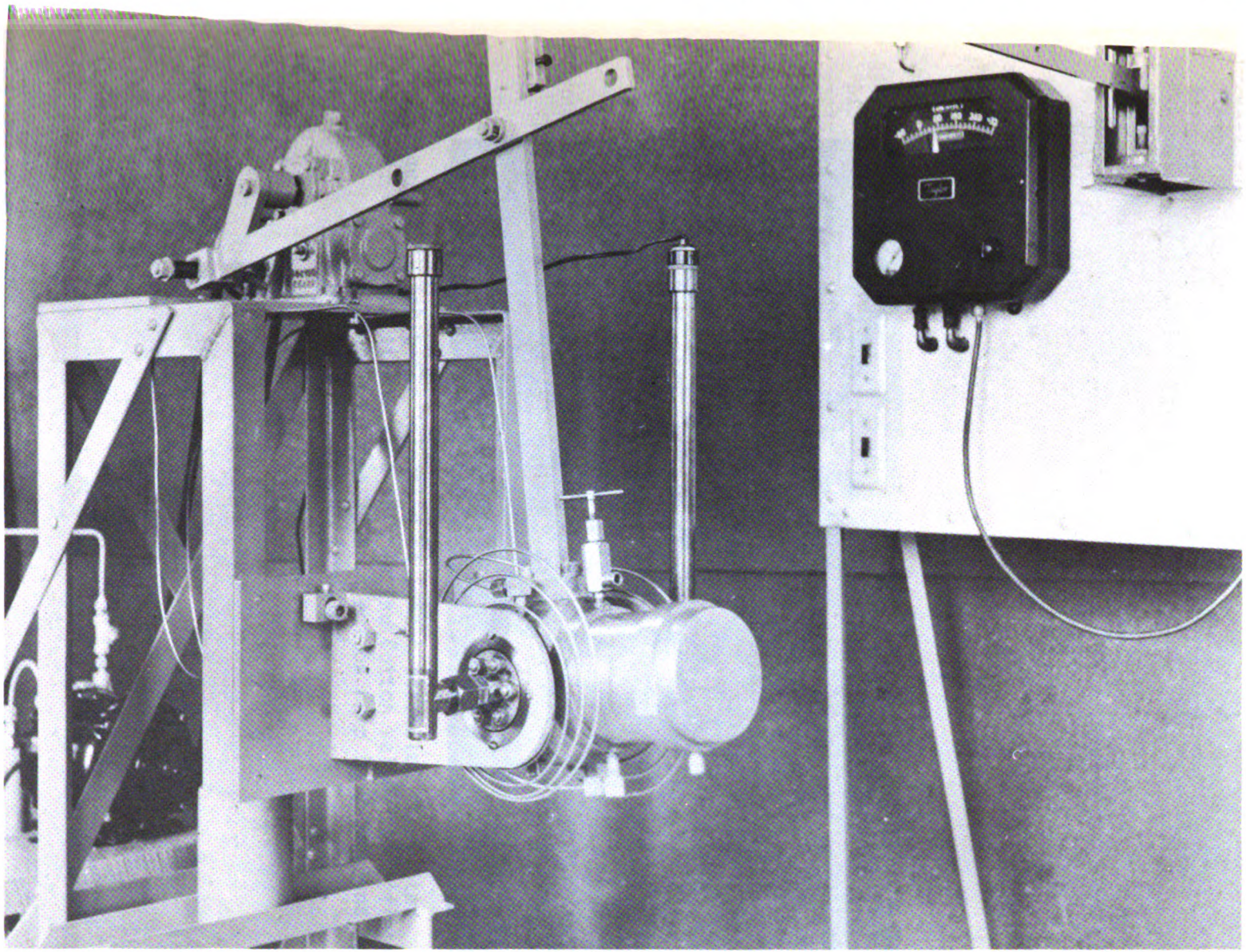

Figure 2. - Windowed cell in its mounting in foreground, with rocker arm attached to motor reduction gear. The vertical tube on the left, attached to central axis of cell, permits visual inspection through a special glass window of fluid meniscus within. The vertical tube on the right provides a source of illumination through another window on the opposite wall of the cell.

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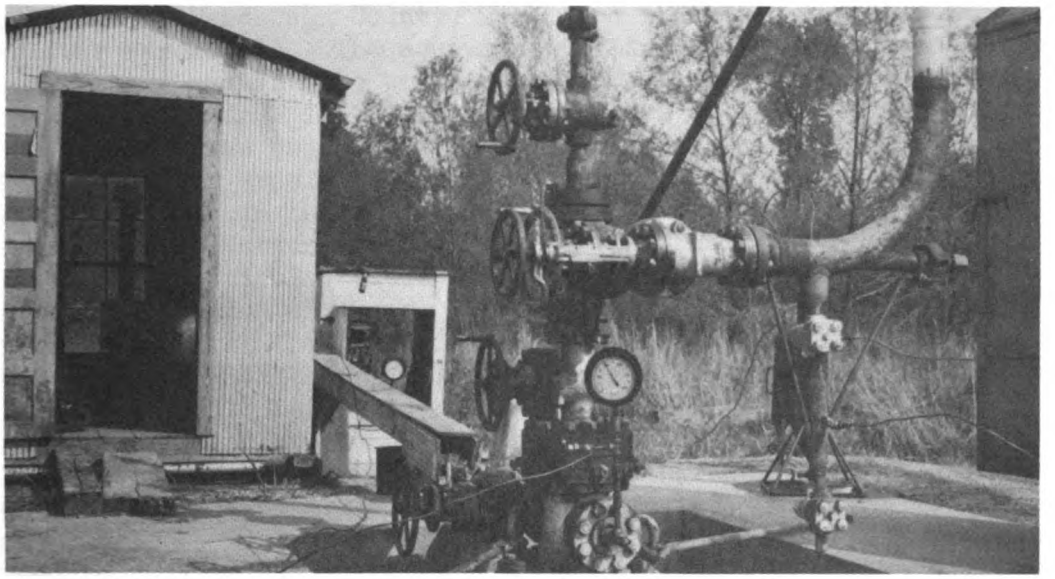

Figure 3. - Inhibitor injecting equipment assembled for winter operations at a well in the Cotton Valley, La., field. Tubing insulated from injection pump in background to wellhead to prevent freezing.

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Gratifying progress was made in the study of the nature of the corrosion and in the development of an inhibitor and of a method of treating gas-condensate wells. The advantages of using sodium chromate, which is being tested under actual operating conditions in wells, have been described 13/.

In the laboratory tests, sodium chromate inhibited the corrosion of steel by various agents present in gas-condensate fluids. Among these are carbonic acid, several of the fatty acids (such as formic, acetic, propionic, butyric, and valeric), and phenol. Tests also showed that sodium chloride, a common constituent of oil-field brine, had slight effect upon the rate of corrosion of steel in propionic and carbonic acid solutions.

Upon the basis of data developed from laboratory tests, sodium chromate was tried experimentally by Bureau of Mines engineers in two wells, one in the Opelika field, Henderson County, Tex., and the other in the Cotton Valley field, Webster Parish, La. The equipment for injecting an aqueous solution of sodium chromate against the wellhead pressure into the annulus of a well at Cotton Valley is shown in figure 3. The rates at which sodium chromate in aqueous solution was injected were varied to determine changes (1) in rates of corrosion of steel test specimens in the flow stream and (2) in the concentration of iron in the produced water. It was found that sodium chromate formed obstructions in the flow string under certain operating conditions, but this difficulty was overcome by increasing the amount of water injected with the sodium chromate. Enough additional water was provided to saturate the fluid from the formation as it entered the tubing and thus prevent evaporation of the inhibitor solution. Some of the benefits of corrosion control were lost while information was being collected on the nature and causes of the formation of the deposit in the tubing. Nevertheless, very desirable benefits were obtained as compared with rates of corrosion measured at the well before sodium chromate had been injected. The rate of corrosion, based on the corrosion of test specimens and on iron in the effluent water, was reduced to as little as 2 percent of the original.

Following preliminary investigations in the laboratory, a trial of a novel method of using an inhibitor was run in the field. Solid sticks of sodium chromate were "lubricated" into the well tubing and allowed to fall to the bottom of the well against the flow of the fluid being produced 14/. This expedient was devised for use in gas-condensate wells where it is impossible to inject an inhibitor into the lower end of the tubing through the annular space between the tubing and casing.

13/ Eilerts, C. K., Carlson, H. A., Smith, R. V., Archer, F. G., and Barr, V. L., Sodium Chromate as an Inhibitor of Corrosion in Gas-Condensate Wells. Presented at the Convention of the Natural Gasoline Association of America, Dallas, Tex., April 17, 1946. Published in the Proceedings of the Natural Gasoline Association of America, 1945-46, Dec. 1946, pp. 51-66.

14/ Eilerts, C. K., Sodium Chromate Effective in Combating Corrosion in Gas Wells; Oil and Gas Journal, May 18, 1946, p. 124.

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Sodium chromate was dried, melted, and cast into anhydrous sticks 1-1/8 inch in diameter by 8 inches in length, weighing approximately 0.6 pounds each. The sticks were fitted with nylon cord ties, heated to 140° F., and dipped into sodium silicate of the same temperature. The silicate formed a slowly dissolving coating for protection until the sticks reached the bottom of the well. In figure 4 the operator is equalizing the pressure in the loading magazine and the well preparatory to dropping sodium-chromate sticks into the well. Tests in the field proved that the sticks could be injected into 2-1/2-inch tubing against the flow of fluid when the mean fluid velocity was 11 feet per section.

Petroleum Engineering Field Studies

Carthage Field

The Carthage, Tex., gas-condensate field was discovered in 1936, although little development occurred until 1938, when a limited market for gas was found and the liquid condensate was trucked from the field. War demand for these liquid components for aviation gasoline accelerated the development of the field to such an extent that the Petroleum Administration for War requested the Bureau of Mines to study the fluid characteristics of the gas condensate and obtain an estimate of the reserves. These data were submitted in two restricted reports to the PAW and operators in the field in March 1944, at which time the field had only 24 wells, including dry holes, and involved an area of about 40,000 acres. Since August 1945, a detailed engineering study has been in progress. Rapid development is occurring, and at present there are more than 200 wells in a productive area extending over more than 250,000 acres. The study of the field is being maintained current with development, and a report will be prepared for publication when data are considered adequate to present reliable estimates of gas and gas-condensate reserves in the reservoir. A survey of bottom-hole pressures and temperatures, needed in the estimation of reserves, has been completed.

Lake Creek Field

The engineering study of the Lake Creek field, Montgomery County, Tex., deals with gas-bearing strata between the depths of 8,800 and 12,000 feet in the Wilcox formation that has been divided into eight producing zones. Each zone consists of one or more producing strata. Since the restricted report was prepared in October 1944 for the Petroleum Administration for War, nine new wells have been drilled in the Lake Creek field. The number of producing wells in the field presently is 22, and there are 5 input wells. Many of the wells in the Lake Creek field were completed to produce through separate flow channels from two zones, and a few wells were completed to produce from three zones.

The extremely low permeability of the oil-bearing strata (25 millidarcys or less) comprising the different reservoirs draws attention particularly to the flowing characteristics of the wells and pressure-production relationships, whereas the high hydrocarbon content of the wet gas (as

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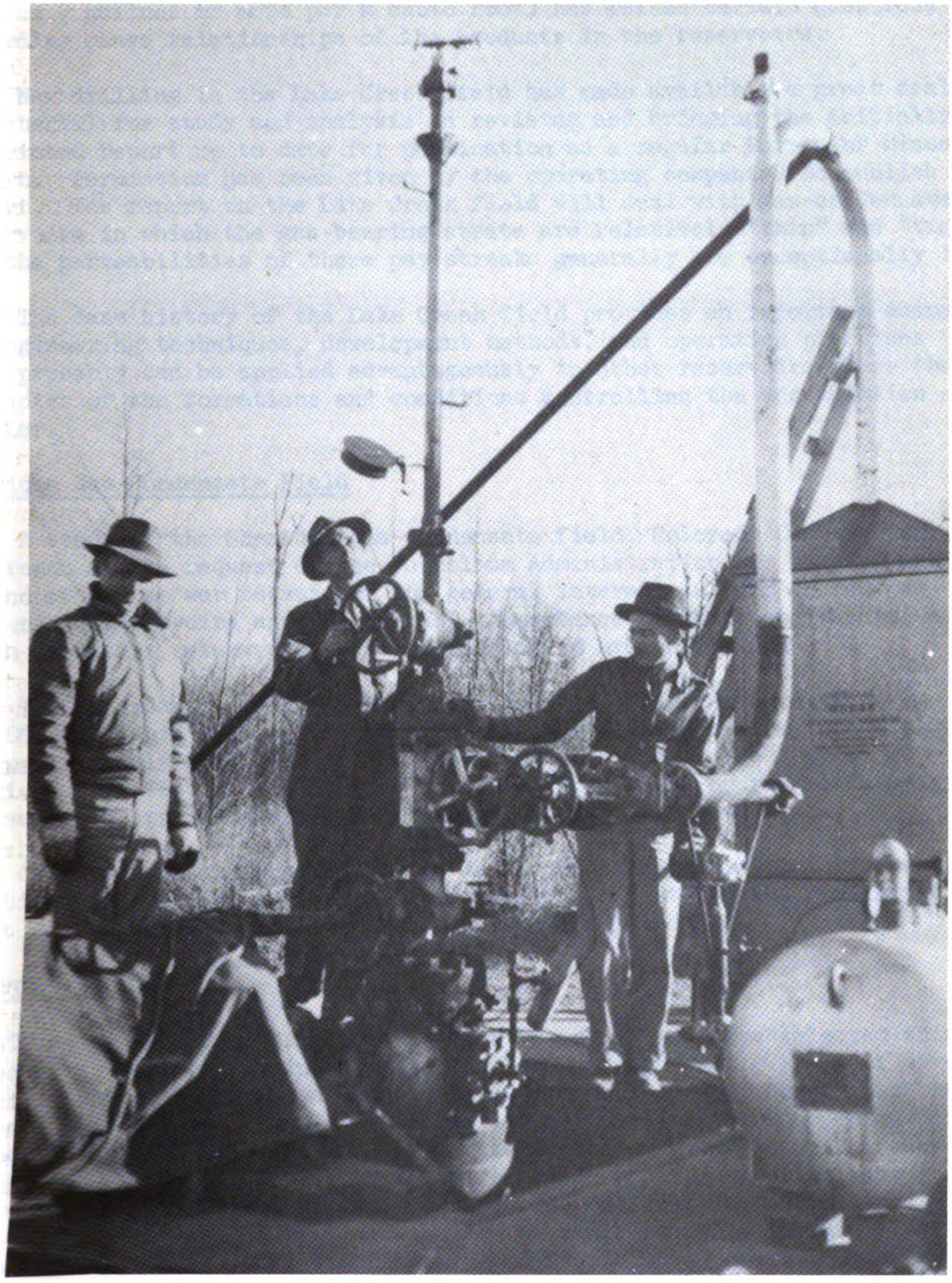

Figure 4. - Operator in the process of dropping sodium chromate sticks into well from loading magazine attached to top of wellhead.

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high as 7 gallons or more per M cubic foot) has raised certain questions regarding phase relationships of the products in the reservoirs.

New drilling in the Lake Creek field has made available a great deal of material for study and analysis in revising and bringing the initially restricted report up to date for publication as a regular Bureau of Mines report. Permission has been given by the operating companies to publish the report. The report on the Lake Creek field will deal with gas-condensate reservoirs in which the gas-bearing strata are relatively "thin" and "tight" and the permeabilities of these pay streaks generally are exceptionally low.

The case history of the Lake Creek field provides an important example of engineering techniques, development methods, and operating practices that probably can be applied advantageously to other reservoirs where the character of the formations and conditions controlling the accumulation are similar.

Sheridan Gas-Condensate Field

A study of the Sheridan gas-condensate field, Colorado County, Tex., was begun at the request of the Petroleum Administration for War and continued after the war because of the general interest in deep-seated gas-condensate reservoirs and the probable importance of these condensate reservoirs as future reserves of gaseous and liquid hydrocarbons.

The Sheridan cycling plant was designed to process a throughput of 100,000,000 cubic feet of wet gas daily from wells dually completed at depths of approximately 9,300 and 10,300 feet, and to return approximately 88 million cubic feet of residue gas to the principal gas-bearing strata at pressures of approximately 3,800 to 4,100 pounds per square inch.

Operation of the Sheridan field is an outstanding example of conservation practices in which no part of the raw product is wasted. The preliminary draft of the Sheridan field report has been completed.

New Hope Field

The New Hope field in Franklin County, east Texas, was selected this year for a petroleum-engineering study, because the first 2 years of development and operation revealed complex and uncommon reservoir conditions that are not well understood. As the crude oil in three of the four reservoirs is undersaturated with gas and the movement of edge water into the reservoirs is impeded by low permeability of the reservoir rocks, the propulsive force driving the oil to the wells was derived, for the most part, from the expansion of the reservoir fluids. The reservoir pressure in three reservoirs has declined precipitously, and many of the wells have ceased to flow by natural forces. An attempt is being made to arrest the decline in pressure in the fourth zone, the Pittsburgh reservoir, by injecting extraneous water through two injection wells.

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Rangely Field

Research regarding the characteristics of the Weber oil reservoir in the Rangely field, Rio Blanco County, Colo., and of the oil in that reservoir is being conducted at Rangely, Colo., and at Laramie, Wyo. This research will provide the oil operators in this field with definite knowledge of these characteristics so that operational procedures may be established to obtain the maximum possible recovery of oil. The analysis of the reservoir and its contents has progressed enough during the past year to indicate the character of the oil-gas solution and the probable reservoir performance.

Bureau of Mines research reveals that the Weber reservoir is the second in the Rocky Mountain area to contain oil of widely varying characteristics. The oil in the top part of the structure, underlying the free gas for a depth of 50 to 100 feet, was saturated with gas (420 cubic feet per barrel) at initial reservoir conditions of 2,550 p.s.i.a. and 154°F. As a result of the gas coming out of solution, 1.23 barrels of this reservoir oil will shrink to one barrel of stock tank oil.

From this zone of gas-saturated oil there is a gradual decrease in the concentration of solution gas to the edge of the field, where the oil has only 230 cubic feet of gas in solution in a barrel of oil with a saturation pressure of approximately 2,000 p.s.i.a. at initial reservoir conditions of 2,860 p.s.i.a. and 162°F. As a result of this gas coming out of solution, 1.15 barrels of this reservoir oil will shrink to 1 barrel of stock-tank oil. The viscosity of the oil in the reservoir varies from 0.8 centipoises at the top to 1.5 centipoises at the edge. The oil as it comes from the wells at the top of the structure has an A.P.I. gravity of 35° and gradually decreases to 33° from wells at the edge of the reservoir.

Special Study of Naval Petroleum Reserve No. 1, Elk Hills Field, Calif.

The United States Navy, in 1945, requested the Bureau of Mines to assist in the wartime development of Naval Petroleum Reserve No. 1, Elk Hills field, Calif., to assure maximum oil production under efficient operation to supply petroleum products in the Pacific theater. Specifically, the Navy desired data on the physical properties of the reservoir oil from the shallow zone, (the most prolific) of the Naval reserve to augment data previously obtained, for the purpose of calculating reservoir performance and oil reserves. Subsurface oil samples for laboratory analysis, reservoir pressures and temperatures on five selected wells, and production gas:oil ratio data on one well were obtained. Casinghead samples of gas were taken for recombination with the subsurface oil samples to form mixtures similar in composition to the initial reservoir oils. The laboratory analyses of the subsurface oil and recombined oil and gas samples included (1) saturation pressures at four temperatures, (2) thermal expansion of each sample while in the liquid phase, (3) compressibility of the liquid-phase sample, (4) pressure-volume relationships at reservoir temperature, (5) differential gas liberation at reservoir temperature, (6) flash-gas liberation data at five gas:oil separator pressures, and (7) pressure-viscosity data at reservoir temperature.

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These field and laboratory data were submitted as progress reports to the Navy and the Unit Operators as each part of the field and laboratory work was completed. A summary compilation of the data contained in the original reports has been supplemented by correlations of some physical properties of the reservoir oil with the A.P.I. gravities of the produced oil and by material-balance calculations relative to one of the oil horizons in the shallow zone. This report has been completed and submitted for publication15/.

Well-Spacing Studies

The problem of optimum spacing of oil wells to determine the minimum number of wells that should be drilled in oil fields to effect maximum oil recovery at minimum cost continues to receive major consideration by engineers of the San Francisco office.

Working closely with the members of the American Petroleum Institute Special Study Committee on Allocation of Production and Well Spacing, oil-production and reservoir data on more than 100 fields throughout the United States were collected and analyzed to determine if the distance between wells is a factor in ultimate oil recovery and upon what characteristics of the oil and the reservoir the relation between oil recovery and spacing depended.

The data collected during the past year were more complete than those available in previous years and included such information, not formerly generally available, as the permeability, porosity, and interstitial water content of the reservoir sands and rocks and formation volume factors that showed for each field the volume a barrel of oil in the stock tanks occupied in the reservoir. Thus, for the first time was it possible to make comparisons on a large number of fields of the relation between the percentage of oil to be recovered ultimately (or the percentage of oil that remains in the reservoir when oil no longer can be recovered at a profit) and well spacing. Such data previously were available on only a limited number of fields, and most early comparisons of ultimate productions had to be made on the less-significant basis of number of barrels of oil recovered ultimately per acre-foot of oil-producing formations.

Studies of Water-Base and Oil-Base Drilling Fluids and Water Contents of Formation Cores

Sands that form reservoirs from which oil is produced originally were laid down in ancient seas, and the pore spaces of the sands were saturated with water. During geologic time, oil replaced some of the water in the sands, but the displacement was not complete, as analyses of cores cut from reservoir sands while wells are being drilled into them indicate interstitial (connate, formation, or native) water contents ranging from about 10 to 50 or more percent of the pore space.

15/ Cook, Alton B., and Shea, G. B., Special Studies of Reservoir Oils in Naval Petroleum Reserve No. 1, Elk Hills Field, Calif.

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In the calculation of oil reserves and in evaluating oil properties, it is necessary to know the percentages of oil and water in the reservoir sands. Such information also assists petroleum engineers and operators of oil properties in determining the optimum procedures for recovering the oil.

As most wells are drilled with water-base drilling fluids and the pressure of the fluid at the drilling bit exceeds the pressure in the formation being drilled, some water from the drilling fluid enters the formation ahead of the drill. Therefore, the relative percentages of oil and water in cores cut from the reservoir sands (usually by special coring tools) differ from the relative percentages of these fluids normally in the reservoir sands. The problem confronting the petroleum engineer, then, is how much of the water found in the cores is formation water and how much is filtrate from the drilling fluid. As means for solving the problem have not yet been perfected, engineers usually are compelled to estimate the relative percentages of oil and water in most reservoir sands.

In an endeavor to perfect a means for determining the contamination of cores by drilling fluids by quantitatively measuring the volume of filtrate that enters reservoir formations ahead of the drill, the Bureau of Mines, in cooperation with the American Petroleum Institute and the Shell Oil Co., carried out a series of tests in the Mercy, Tex., oil field. In these tests an oil-base drilling fluid was used in the well. A tracer consisting of an organic chloride that is insoluble in water, highly soluble in oil, and extremely stable at high temperatures was added to the drilling fluid.

Although the oil-base drilling fluid used in the tests exhibited very low rates of filtration as measured by the accepted standard filter test for drilling fluids, there was excessive contamination of the cores by the drilling fluid. The tests, therefore, failed to give sought-for information on the degree of contamination of formation cores by drilling fluids. Nevertheless, the tests indicated the superiority of oil-base over water-base drilling fluids for reducing the contamination of cores. Several refinements in the manner of conducting the field tests and in laboratory analytical procedure also were suggested by the tests.

Correlations of Physical Properties of Oil

The best known procedures for the development and production of petroleum reservoirs to obtain maximum economic recovery of oil and gas are predicated on a comprehensive knowledge of the physical characteristics of the reservoir and of the contained fluids (oil, water, and gas). The development of methods for determining these physical characteristics included, in recent years, a procedure for "bottom-hole" or subsurface sampling of reservoir fluids for analysis 16/. This reservoir sampling is time-consuming and expensive, and consequently a long-range study was begun to determine the relationships between the physical characteristics of reservoir oils and the properties of oils as produced at the surface.

16/ Grandone, Peter, and Cook, Alton B., Collecting and Examining Subsurface Samples of Petroleum: Bureau of Mines Tech. Paper 629, 1942, 68 pp.

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Bureau of Mines engineers have obtained many subsurface oil samples of widely differing properties. Comparison of this information with distillations of produced oil samples has led to tentative correlations. The study is being continued in the hope that final correlations can be made after detailed data have been obtained on a wide range of oil characteristics and reservoir conditions. This type of research, which must advance "one step at a time", exemplifies a trend in engineering analyses as applied to oil-reservoir performance studies by Bureau of Mines engineers. Paralleling this work is the accumulating of data on initial pressures and temperatures of oil and gas reservoirs. Present-day field engineering studies, such as those being made in the Carthage and New Hope fields in Texas, described in another section of this report, would fall short of their objective if these data were omitted.

Review of Gas-Conservation Practices

Bureau of Mines research on production and conservation of natural gas through pressure maintenance and gas cycling was described in a statement[17] presented before the Federal Power Commission at the Washington hearing. The statement traced the Bureau's pioneering work from 1917, when J. O. Lewis recognized the importance of natural gas in the efficient recovery of oil to the present-day concepts of fluid-energy relations. The important research work conducted during the past 10 years by the Bureau's physical chemists on phase relations of hydrocarbon gases was recounted because of its application to the large reserves of gas that exist under high pressure in the deep-seated reservoirs.

As the Federal Power Commission has evinced an interest in a better utilization of casinghead or solution gas after it has performed useful work in driving crude oil through the reservoir rocks to the wells and lifting it to the surface of the ground, the possibility of conserving casinghead gas through pressure maintenance in oil-producing reservoirs was discussed. After explaining the properties of reservoir fluids and reservoir mechanics, it was concluded that pressure maintenance is most effective when applied to dissolved-gas and gas-cap drive reservoirs, or to water-drive reservoirs in which the rate of water encroachment keeps pace with the withdrawal of oil and gas. Under most conditions, it was pointed out, pressure maintenance by the injection of gas aids in producing more oil with lower lifting cost and in a shorter period of time, and if carried to the end point will result in storage of natural gas that can be marketed as fuel. Because pressure maintenance by the injection of casinghead gas has not been adopted as widely as would be expected for such a beneficial practice, the impeding obstacles and legal difficulties were emphasized.

SECONDARY RECOVERY

The importance of secondary-recovery operations in the national petroleum economy has been emphasized by many members of industry. Illustrative

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17/ Carpenter, C. B., Bureau of Mines Research on Production and Conservation of Natural Gas Through Pressure Maintenance and Gas Cycling: A Statement before the Federal Power Commission Docket G-580, Washington, D. C., June 17, 1946.

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are statements to the Senate Special Committee Investigating Petroleum resources by H. M. McClure, president of the National Stripper Well Association and chairman of the State Oil Board of Michigan, and Don T. Andrus, immediate past president of the Pennsylvania Grade Crude Oil Association and Pennsylvania's representative on the Interstate Oil Compact Commission18/.

Mr. McClure said in part:

> The most recent authoritative survey of stripper well production was made by the Interstate Oil Compact Commission and the National Stripper Well Association covering the year 1944. * * *.
>
> It discloses that, of the 412,851 producing oil wells in the nation, 296,388, or 71.8 percent, are classified as stripper wells. In 1944, these stripper wells produced 217,041,621 barrels of oil or 12.9 percent, out of a total United States production of 1,678,376,000 barrels. Average daily production per well was 11.1 barrels for all oil wells and 2.0 barrels for the stripper wells.
>
> The number of stripper wells producing in 1944 was 3,107 greater than in 1942, when the previous survey was made. The survey likewise shows that the stripper wells produced approximately 14 million barrels more in 1944 than in 1942. This oil was sorely needed for the successful prosecution of the war when flush and semiflush wells in many parts of the country were being produced at rates above their maximum efficient rates of production.
>
> In fields now developed we have a total of 298,000 stripper wells with reserves conservatively estimated at 4 billion barrels, - 20 percent of our nation's total reserves, which approximate 20 billion barrels.
>
> The preservation of marginal or stripper-well properties by the application of secondary recovery methods is a conservation measure of great importance and one that should be carefully considered in the formulation of a national oil policy.

Mr. Andrus stressed the need for conserving these resources, by stating:19/

> Secondary recovery is the re-energizing of these inert oil reservoirs with a replacement force (high-pressure air, gas or water) to again put the oil in movement. Oil produced from a

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18/ Mimeograph statements distributed by the I.P.A.A., briefed in The Independent Monthly, vol. XVI, No. 12, April 1946, pp. 10 and 11.

19/ See footnote 18.

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reservior before the new technique of pressure maintenance was developed was about in this proportion: about 20 percent producible by the original gas pressure, about 25 percent by secondary recovery methods. The rest, comprising more than half the original oil in the sand, the industry has given very little thought toward recovering.

Pointing out that the surface of the possibilities of secondary recovery "salvage" has been barely scratched, he concluded: "The United States Government should be a leader, not a laggard, in the effort to conserve the residual oil areas and to promote secondary recovery."

The Bureau of Mines has been active in the study of secondary recovery for 30 years, the results of the first work by J. O. Lewis 20/ having been published in 1917, and in recent years it has stressed such work not only to increase the production of crude petroleum but, which is equally important, to prevent the premature abandonment of wells in "stripper" and marginal areas.

Methods of Increasing the Recovery of Oil

Field Studies

Secondary-recovery projects in limestone reservoirs are not numerous and involve problems not usually met in sandstone formations. To stimulate interest in the application of secondary-recovery methods in limestone producing strata, a report was published 21/ that gave in detail the results of gas injection in the limestone strata in the Griffin and New Harmony oil fields in Indiana and Illinois. These projects represent the first large-scale gas-injection operations in limestone reservoirs in the deeper fields of the Illinois basin. Approximately 85,000 barrels of oil was obtained in 2 years by injecting 500 million cubic feet of excess gas through seven injection wells. The report contains a discussion of the development, production practices, and reservoir conditions in the Griffin and New Harmony fields and shows the estimated oil gained from the producing wells affected by gas injection. It also includes data on the time elapsed between initial gas injection and increase in rate of oil production in affected wells.

A report on water-flooding practices in north Texas was completed 22/. Water-flooding in Texas has been confined chiefly to the old "shallow" fields in eight counties of the north-central part of the State. These

20/ Lewis, J. O., Methods for Increasing the Recovery from Oil Sands: Bureau of Mines Bull. 148, 1917, 128 pp.

21/ Riggs, C. H., Gas Injection into the McClosky Limestone in the Griffin and New Harmony Oil Fields, Indiana and Illinois: Bureau of Mines Rept. of Investigations 3818, 1945, 28 pp.

22/ Grandone, Peter, Jessup, D. A., and Taliaferro, D. B., History of Water-Flooding of Oil Sands in North Texas: Bureau of Mines Rept. of Investigations 3906, 1946, 117 pp.

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operations center mainly in two oil-producing districts - the Burkburnett-Wichita Falls district in Wichita County and the Olney-Prideaux district in Young County.

Although the first water-flooding project in the area was started in 1936, the practice was not widely adopted by North Texas operators until 1943. This was due in part to the difficulty of successfully flooding the lenticular sands from which many north Texas fields produce. However, by the end of 1944 there were 33 active and 5 discontinued water-flooding projects - a total of 38 projects in the area, with a total development of 1,970 acres. To December 31, 1944, these projects had produced 1,140,956 barrels of oil by the injection of 12,061,997 barrels of water. This recovery of 579 barrels of oil per acre is not to be construed, however, as indicative of the efficiency of the operations, as many of the projects are new and had not reached their peak rate of production.

In the north Texas stripper area, comprising 10 counties, there are 16,000 wells that are barely paying the cost of operation under the existing methods of production. The results reported indicate that many millions of barrels of oil can be recovered at a profit from these old oil-producing areas by the application of water-flooding practices.

A detailed engineering study of the Delaware-Childers field in Nowata County, Okla., were completed. The field was discovered in 1907 and was operated by primary production methods until 1913. In that year gasoline plants were constructed, and most of the field was placed under vacuum. Air and gas repressuring was begun in 1925 and was expanded to include the entire field during the next few years. Figure 5 is a composite curve of oil production showing effect of gas injection upon a small area (568 acres) in the Delaware-Childers field. The time during which the field was operated under vaccum is included in that part of the curve representing the primary method production period (23 years), which shows a total gross production of 4,651 barrels per acre, whereas the same properties have produced 4,404 additional barrels of crude petroleum per acre in 14 years by secondary recovery operations in which gas injection methods were employed.

A cooperative study of the West Red River field (Texas-Oklahoma boundary) by engineers of the Bureau of Mines and the Geological Survey has been proposed. This is a relatively small, lenticular, sand field that was developed and operated under a receivership from 1920 to July 1, 1924, when the operation was transferred to the Secretary of the Interior as Trustee during the period in which claims were to be adjudicated, leases granted, and the properties returned to the lawful claimants. Supervision of the properties by the Bureau of Mines ended on the morning of July 1, 1925, and subsequent supervision from that date has been under the direction of the Geological Survey in accordance with the Leasing Act governing operations on Federal land. Production and cost records were kept for each individual well until December 1, 1925.

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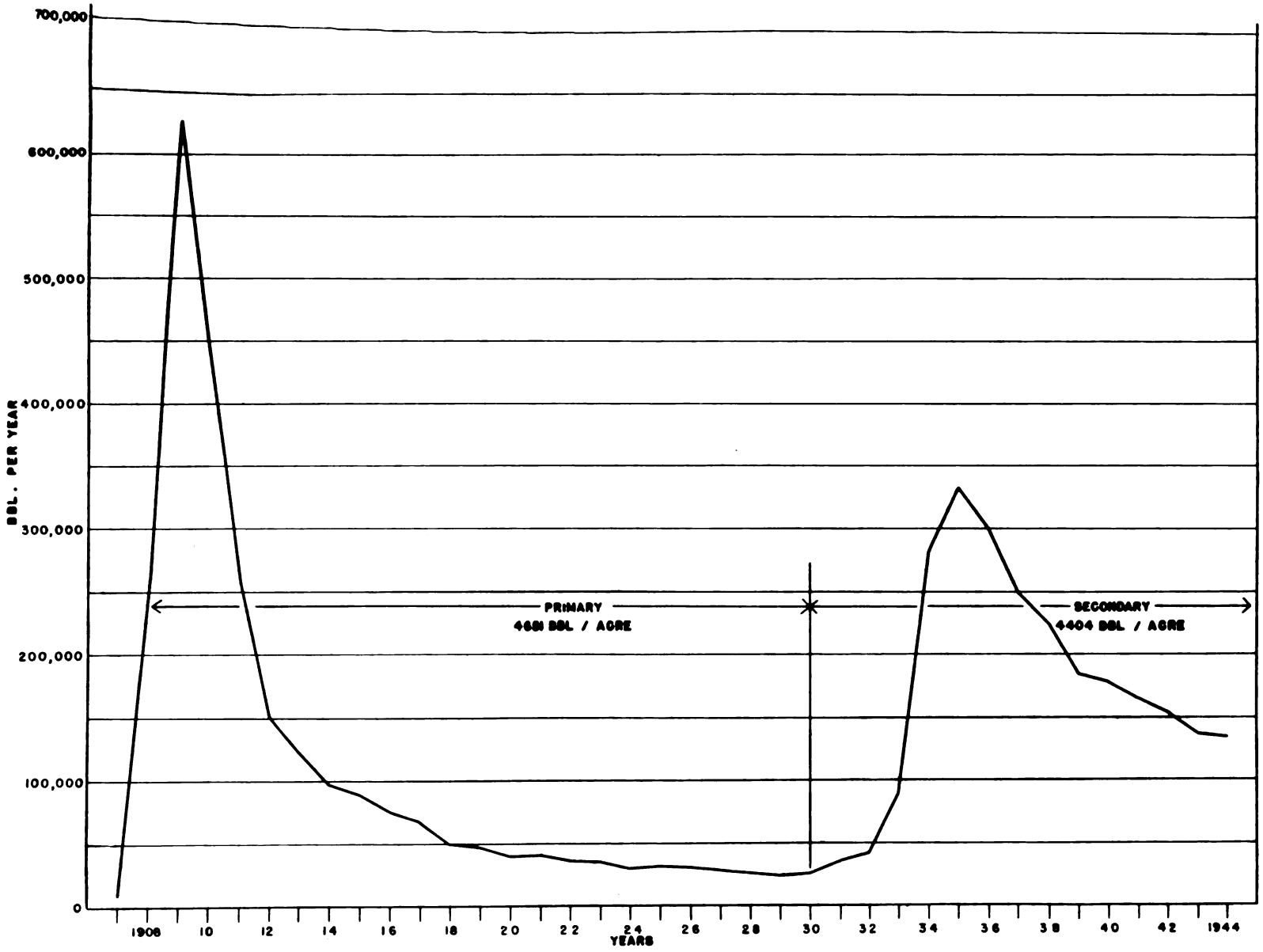

Figure 5. - Composite curve of oil production showing effect of gas injection on 568 productive acres, Delaware-Childers field, Nowata County, Okla.

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The early drilled wells (approximately 31) were bottomed in the upper half of the producing-sand section; production records show the results of shooting the oil-bearing strata one or more times with light shots (4 to 10 quarts) of nitroglycerine and the results of deepening the wells, vacuum operations, and later the results obtained by repressuring, drilling new wells, deepening old wells, and shooting the producing formation with relatively larger amounts of nitroglycerine.

The West Red River field has virtually reached the economic limit of production by primary and even secondary methods of repressuring with gas and air. Perhaps the most likely method of increasing production and extending the life of the wells in this field is by water-flooding. The detailed engineering study being conducted at present should be helpful in shallow reservoirs that have been virtually depleted by conventional production methods.

Petroleum Engineering Studies in the Applalachian Region

During the early part of the fiscal year 1946, a need developed for data on the temperature of oil and gas reservoirs in the Appalachian region. This brought about a comparatively extensive survey of earth temperatures in wells of New York, Pennsylvania, and West Virginia. During the summer and fall of 1945, earth temperatures were measured in about 50 wells by means of a recording thermometer, which was lowered into and withdrawn from the wells by means of reeling machinery. For some time many petroleum engineers have been concerned about the possibility that some oils might be immobilized in sands because of low reservoir temperatures. Consequently, each time the temperature of an oil reservoir was measured, a sample of produced oil was obtained, and later the absolute viscosity of the oil samples was determined at appropriate reservoir temperatures in the laboratory. A report 23/ covering these data was prepared and published in a trade journal in May 1946.

A report 24/ in press outlines the progress on the study of flowing oil wells on air-gas injection projects in the Oil City-Pleasantville, Pa., area. This work was begun in July 1943, when an operator asked for assistance in designing a siphon to flow water that was accumulating in a gas well. The initial objective of this study was to devise means to siphon-flow intermittently, rather than to pump intermittently, the oil produced on air-gas injection projects, utilizing the energy in the gas that accompanied the oil into the well bore to flow the oil to the surface, rather than dissipating most of the energy in the gas, as was customarily done when pumping wells.

23/ Tignor, E. M., Subsurface Temperatures and Viscosity-Temperature Relationships of Crude Oils in the Appalachian Region: Producers Monthly, vol. 10, No. 7, May 1946, pp. 12-18, 10 figs.

24/ Grant, Bruce F., and Bossler, Robert B., Experimental Flowing of Oil Wells on Air-Injection Projects in Pennsylvania: Producers Monthly, vol. 10, No. 9, July 1946, pp. 38, 40-42.

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During fiscal year 1946 this research was expanded, and it now covers the study of 77 wells equipped with siphon flowstrings on 18 air-gas injection projects operated by seven companies. In the field studies, time was devoted to designing siphon flowstrings for new installations, gathering pertinent data, and maintaining orifice flow meters to record the gas produced during intermittent flowing of wells. In the laboratory, a model well with casing and tubing of transparent plastic was designed, constructed, and operated to ascertain pertinent data useful in designing siphons for use in oil producing wells.

The report "Oil-Well Reconditioning in Southwestern Pennsylvania, West Virginia, and Southeastern Ohio" was in the final stages of completion at the end of the fiscal year 1946.

Oil Recovery from "Black Sands"

In many oil fields in eastern Kansas, parts of the cores of the oil-bearing formation may appear to be unusually dark in color and highly saturated with oil. These "black-sand" sections vary widely in thickness throughout any given field; in some places the black sand represents almost the entire formation thickness, and in other nearby wells it may be entirely missing. Saturation determinations made on "black-sand" cores by retorting often indicate the presence of 800 to 1,000 barrels of oil per acre-foot of sand, although determinations made by extraction methods usually indicate much lower saturations. When the cores are tested to determine the amount of oil that can be recovered from them by water flooding, it usually is found that no appreciable amount of water can be forced into them at pressures up to 100 pounds per square inch, and that no oil can be recovered.

A representative core sample was obtained from the Squirrel sand in the Paola Shoestring field, Miami County, Kans. The records showed that the well penetrated 41 feet of "sand." Laboratory flooding tests proved that no oil could be recovered from samples from the bottom 13 feet of the core, although retort saturation tests indicated the presence of 760 to 850 barrels of oil per acre-foot of sand. The porosity of this section was found to range from 17.9 to 19.7 percent. Detailed laboratory analyses were made of the "hydrocarbons" contained in the core, and, through the courtesy of the State Geological Survey of Kansas, a petrographic study was made of another specimen of black sand from the same cores. Similar but less complete tests also were made on three samples of black sand from the Quitman field, Wood County, Tex. The results of these studies25/ demonstrated that the organic material in many of these "black sands" should be classified as "asphalt" rather than as "crude oil." The importance of this conclusion is shown by the fact that retort saturation determinations indicate a "reserve" in these sands of many million barrels, which is largely nonrecoverable if it is asphalt instead of crude oil, as is believed usual.

25/ Taliaferro, D. B., and Stanfield, K. E., Asphaltic Sands Found to Occur in Oil Fields: Bull. of Am. Assoc. of Pet. Geol., vol. 30, No. 4, April 1946, pp. 617-619; also, Producers Monthly, vol. 10, No. 6, April 1946, pp. 18-19.

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Laboratory Research on Reservoir Drainage

In June 1944 a secondary-recovery research program was begun with a laboratory experiment designed to determine the relative quantities of oil that could be recovered from a sand by initial gravity drainage at reservoir temperature and the subsequent application of heat to the sand reservoir.

At the end of 12 months following the placing of the laboratory model "on production", all the oil that would drain by gravity was produced and amounted to 57 percent of the original oil in place. Efforts to recover additional oil by air drive were unsuccessful. Heat then was applied in a tunnel beneath the oil reservoir by means of an electric element, and the temperature of the tunnel was increased by 50°F. increments to 234°F., or 150° above the reservoir temperature. Temperatures of the sand directly above the tunnel became stabilized at approximately 185°-190°F. Reservoir temperatures near the sides of the box, however, leveled off at 92°-94°F. Only 0.044 liter of additional oil was produced as a result of the application of heat during a period of 5 months, compared with a total recovery of 38.036 liters by gravity drainage at 84°F. These results give evidence of the limitations of applying heat in a tunnel beneath the reservoir to raise the temperature of the reservoir for the purpose of recovering additional oil from sands from which most of the oil has drained by gravity.

Recovery of Oil from Outcropping Bituminous Sandstones by Hot-Water Washing

Studies initiated in July 1943 to develop a practical method for recovering oil from the bituminous sandstones or "tar sands" of California continued at the San Francisco office. The studies have been concentrated on the application of the hot-water-separation process to the outcropping bituminous sandstones from the Edna area in San Luis Obispo County, Calif. Many laboratory data have been obtained on the factors involved in the process that affect its efficiency, and a method of separation adapted to the Edna bituminous sandstones has been developed.

The process consists, broadly, of four operations: (1) Water-washing the bituminous sandstone to remove soluble iron salts, (2) forming a frothy pulp by heating and mixing the bituminous sandstone with alkaline reagents and a diluent, (3) separating the oil from the disintegrated sandstone by flotation, (4) eliminating the water, sand, and silt from the flotation-unit oil froth. The collected oil contains approximately equal parts of bitumen and diluent. In a commercial plant, the diluent would be recovered by distillation for re-use in the separation process before refining the bitumen for desired products.

Recovery of Wax from Crude Petroleum Wastes

Oil-field waste emulsions are oil and water mixtures that do not respond to conventional demulsifying treatment and which are used for emulsified crude oil from wells. These waste emulsions are very stable, have high salt

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and dirt content and high melting or flow temperatures. Treating and handling are difficult; therefore, the emulsions are regarded by producers as economic wastes, to be disposed of by burning or impounding. The oil content of the emulsions generally ranges between 30 and 70 percent, and the emulsions also contain high-melting-point paraffins; the recovery of oil and wax from these wastes therefore would add materially to the conservation of a natural resource.

A process was developed in the laboratory that was simple and effective in recovering oil from waste emulsions. Analysis shows the recovered oil to be similar to "topped" or partly "topped" crude oil, and it therefore is good refinery stock. To develop the process further, a pilot plant was built near El Dorado, Kans. (fig. 6).

The pilot plant, which has a treating capacity of approximately 15 barrels an hour, is described in detail in a recent Report of Investigations 26/. This plant, which was built beside a disposal pond containing highly weathered emulsion, utilized material having 40 to 60 percent "B. S. and W." and about 4,000 pounds of salt per thousand barrels of emulsion. The purified oil contained 0.5 percent "B. S.", no water, 8 to 12 pounds of salt per thousand barrels, and an average of 17 percent microcrystalline wax.

The report discusses the physical characteristics of waste emulsions, more particularly those run to disposal pits and storage ponds. The method for the recovery of a clean wax-bearing oil and the equipment used in the process are described. The process depends upon proper destabilization, very intimate mixing of the emulsion and the demulsifying chemical, heating to the correct temperature (higher than is usually employed), followed by rapid settling of the salt water and foreign material.

Two methods of separating the clean oil from the emulsion were tried - hot settling and mechanical filtration. Data on the first method show that more than 90 percent of the wax-bearing oil in the waste emulsion is recoverable. Recovery by mechanical filtration was studied, and data on the economics of the process were collected.

Commercial uses for high-melting point wax (160° to 215° F.) have increased steadily in recent years, probably the most outstanding present uses being the preservation of foods and in the manufacture of synthetics.

Core and Water Laboratory

The "core and water" laboratory maintained at the Bartlesville Station tests oil-field "core samples" to supply engineers engaged in secondary-recovery and primary-production studies with information on the physical and chemical characteristics of the producing strata. Mineral analyses of surface and subsurface waters and miscellaneous chemical analyses also are made.

26/ Horne, J. W., Watkins, J. W., Matzick, A., Recovery and Utilization of Oil from Oil-Field Waste Emulsion: Bureau of Mines Rept. of Investigations 3869, 1946, 18 pp.

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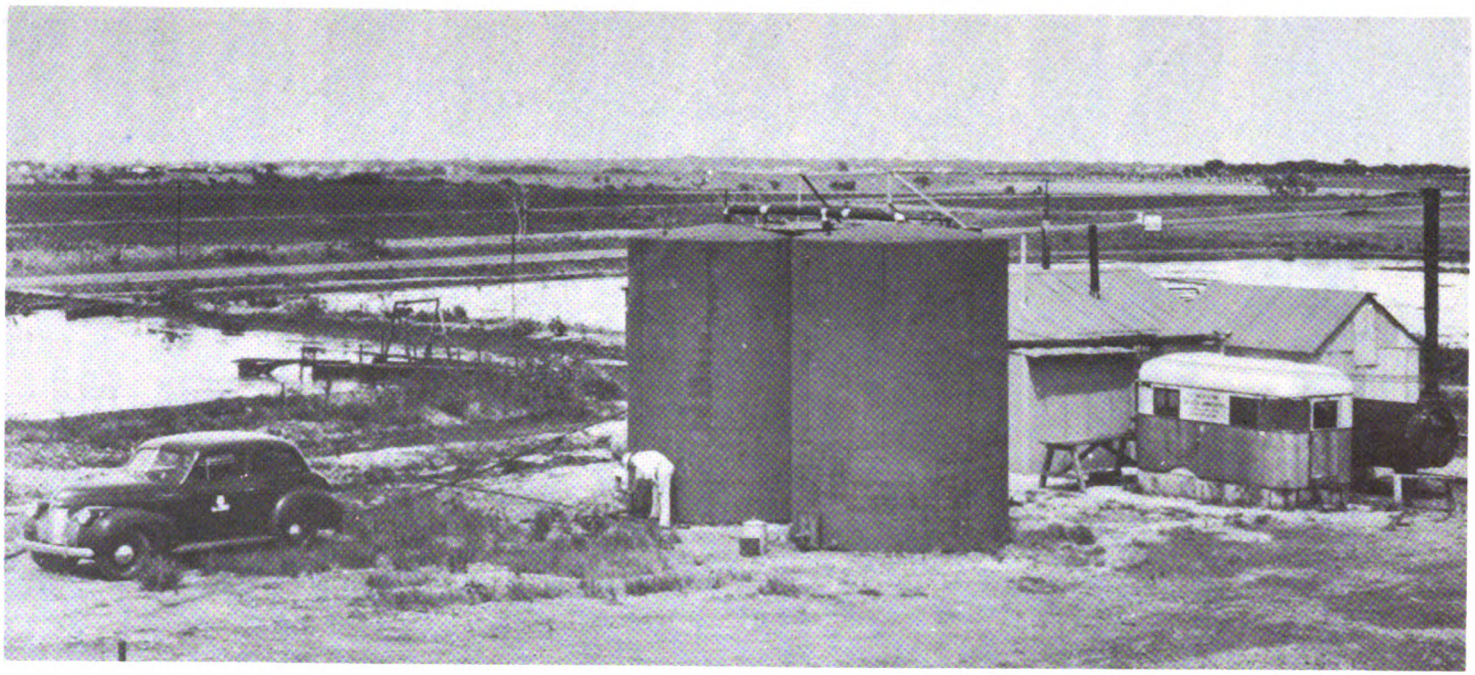

Figure 6. - Pilot plant near El Dorado, Kans., for recovery of wax distillate from oil-field waste emulsion.

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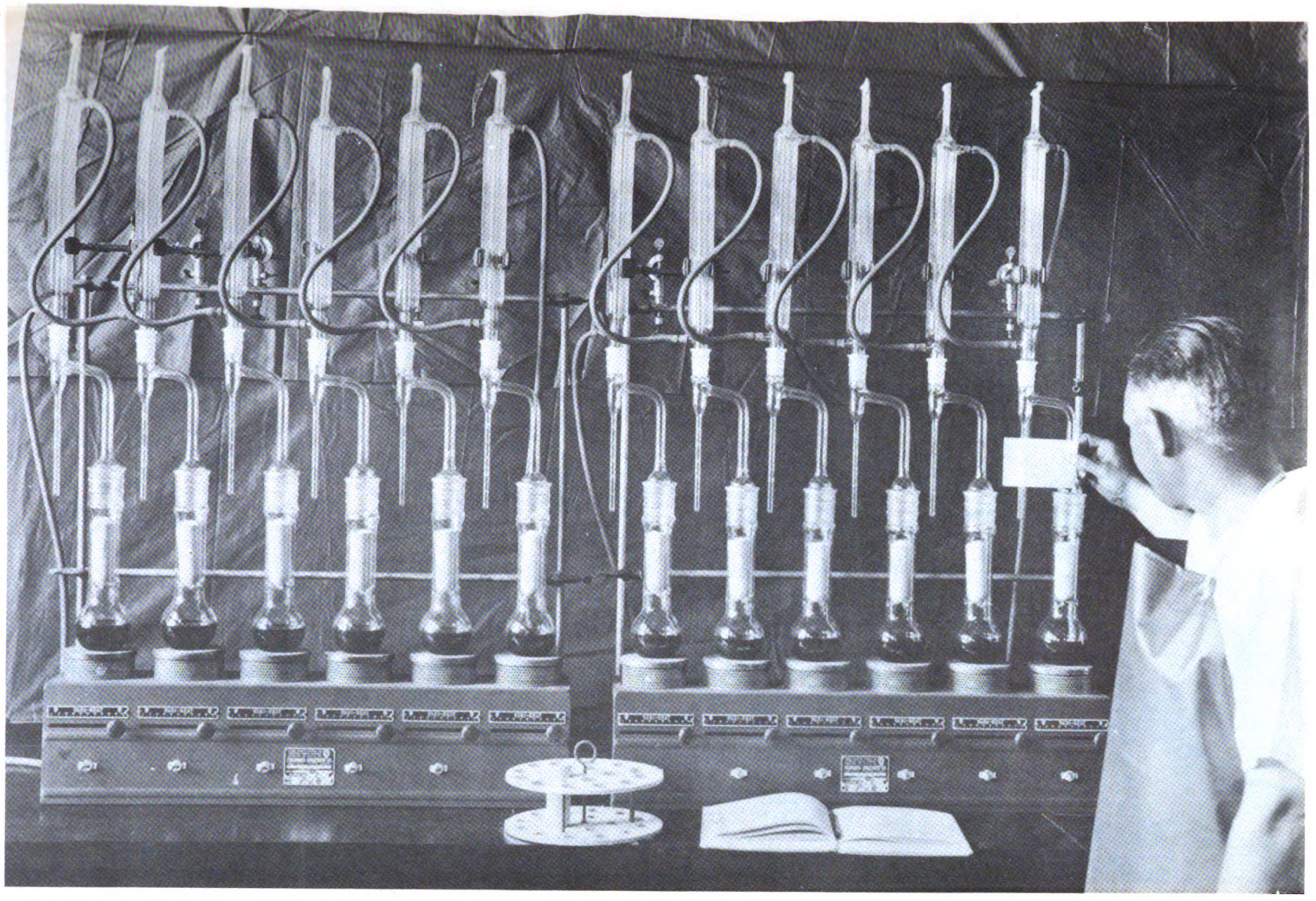

Figure 7. - Bank of extraction units used in the Bureau of Mines core laboratory for determination of oil and water saturation of oil-field cores.

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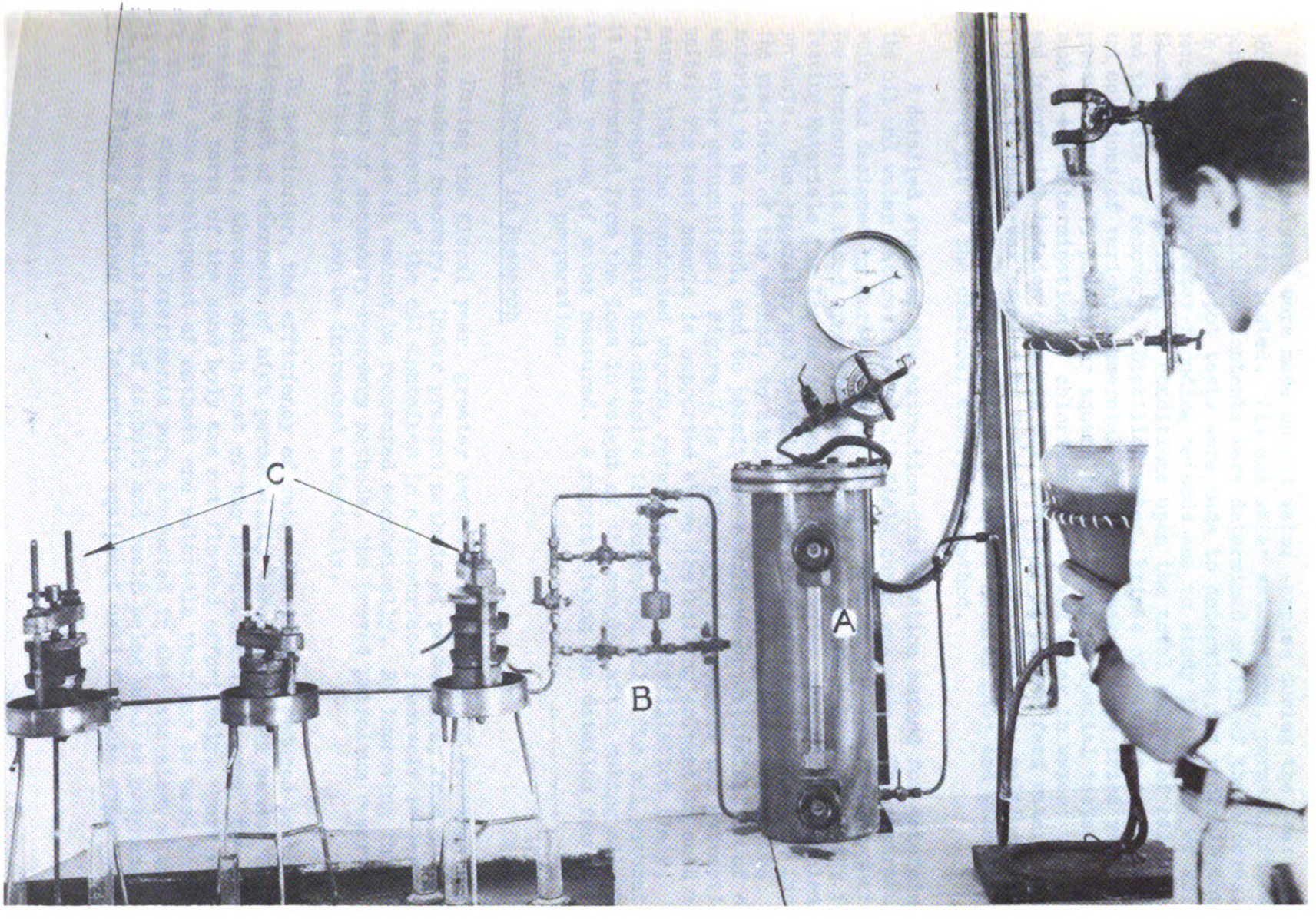

Figure 8. - Laboratory apparatus for study of selective plugging in oil sands: A, Pressure container for deaerated brine solution; B, manifold and connections for introducing "plugging" materials; C, specially designed core holders.

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Mineral analyses were made on 133 water samples during the year, and 386 core samples were tested. Oil and water saturations, permeabilities, porosities, and chloride contents were determined on 333 of these cores. On the other 53, flood-pot tests were made to determine the probable total recoverable oil by water-flooding methods and to study the effect of various flooding media and flooding conditions upon the total volume of oil recovered and the rate of recovery. Distilled water, brines of various concentrations, and solutions of various commercial emulsion breakers were tried with pressures up to 75 pounds per square inch. Numerous special tests were made, such as the determination of chlorides, dirt, and water in waxes; viscosity and interfacial tension of crude oil; nitrates in boiler feed water; wax content of crude-wax samples by fractional crystallization; melting points of wax fractions; hydrogen sulfide content of natural gas; and gasoline in natural gas by the charcoal adsorption method.

A detailed study of the extraction-distillation method for determining the oil and water saturations of oil-field cores was made. The apparatus, which was designed by Bureau engineers, has been in use for several years. The procedure is based upon the method adopted by the American Society for Testing Materials for the determination of the water content of petroleum products. The apparatus and technique have been altered slightly to increase the precision of the method, to adapt it to the characteristics of the material to be tested, and to permit the simultaneous determination of oil and water saturations. Figure 7 is a close-up of a bank of the extraction units. The test sample is supported above the boiling solvent in such a manner that the condensed vapors, returning to the distillation flask, flow through the sample and dissolve the contained oil. The oil saturation is determined from the loss in weight of the sample, after making allowance for the volume of water measured. A report giving the detailed results of this work is in preparation.

Recent Trends in Research

During the fiscal year, greater emphasis was placed on research relating to secondary recovery. Under present methods of production, from 30 to more than 50 percent of the oil contained in a subsurface reservoir is left in the ground, as it cannot be recovered economically. By improving the efficiency of secondary-recovery methods, the proved petroleum reserves of the United States can be increased materially.

In particular, the efficiency of water flooding is reduced by the development of channels of high permeability through the oil sand. Because of these channels, through which most of the injected fluid passes, the less permeable parts of the sand body are not flooded effectively. Work was begun on the development of methods and materials that may be used to seal off these channels. Experiments were conducted in the laboratory with oil-field cores, emulsions of asphalt and resin being used as plugging media. Figure 8 shows the laboratory equipment used in these experiments.

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Although water-flooding methods have been used for about 25 years, there still are diversified views regarding the most efficient injection pressures and rates of injection. Investigation of this problem was initiated, and equipment was obtained to test the behavior of water-input wells. Also, a method measuring, at a reasonable cost, the rate at which each unit thickness of sand penetrated by a water-input well is taking fluid is an outstanding need in water-flooding operations. Without knowledge of the input profile, remedial measures are carried out blindly, and, when completed, there is no positive method of evaluating the results. A device to be used for this purpose was designed and construction of it was begun.

Steps were taken to introduce in the Mid-Continent the practice of flowing small wells on gas-injection projects. This procedure, developed by Bureau of Mines engineers in the eastern fields, will reduce the cost of operation and prolong the life of gas-injection projects.

The foregoing items suggest the trend in exploratory thinking and action by engineers of the Bureau with respect to oil extraction from partly depleted fields. The need is recognized, also, for greater emphasis on research by physical chemists to explain and make use of the phenomena that are manifest when oil and water come in contact (the interfacial relations) and the surface phenomena existing between the reservoir rocks and the fluids contained in them.

PETROLEUM CHEMISTRY AND REFINING

The current broad objective of the research in petroleum chemistry and refining is to obtain a complete picture of the availability of fuels for all types of internal-combustion engines. This includes motor and aviation gasolines, Diesel fuels, and gas-turbo fuels. To attain this objective, all possible qualitative and quantitative data must be determined and compiled on (1) raw materials, such as crude oils, natural gasoline, condensates and synthetic fuels; (2) relationships between fuel compositions and properties, engine performance, and specifications; (3) refinery processes and capacities.

The method of group attack proved so successful in handling war assignments that it is being continued at Bartlesville, Okla., and Laramie, Wyo. Each group of investigators, working on an individual problem, is supervised, so that data obtained by the several groups can be coordinated to provide complete and well balanced answers to the broad problems involved.

The following discussion of the year's work is presented under captions that indicate the group organization for petroleum chemistry and refining research in the Bureau of Mines.

Experimental Sample Processing

Continuous Distillation

There are several requirements that samples for petroleum research should meet. Among these are (1) authentic source, (2) sufficient quantity, (3) accurate quantitative background data, and (4) complete processing

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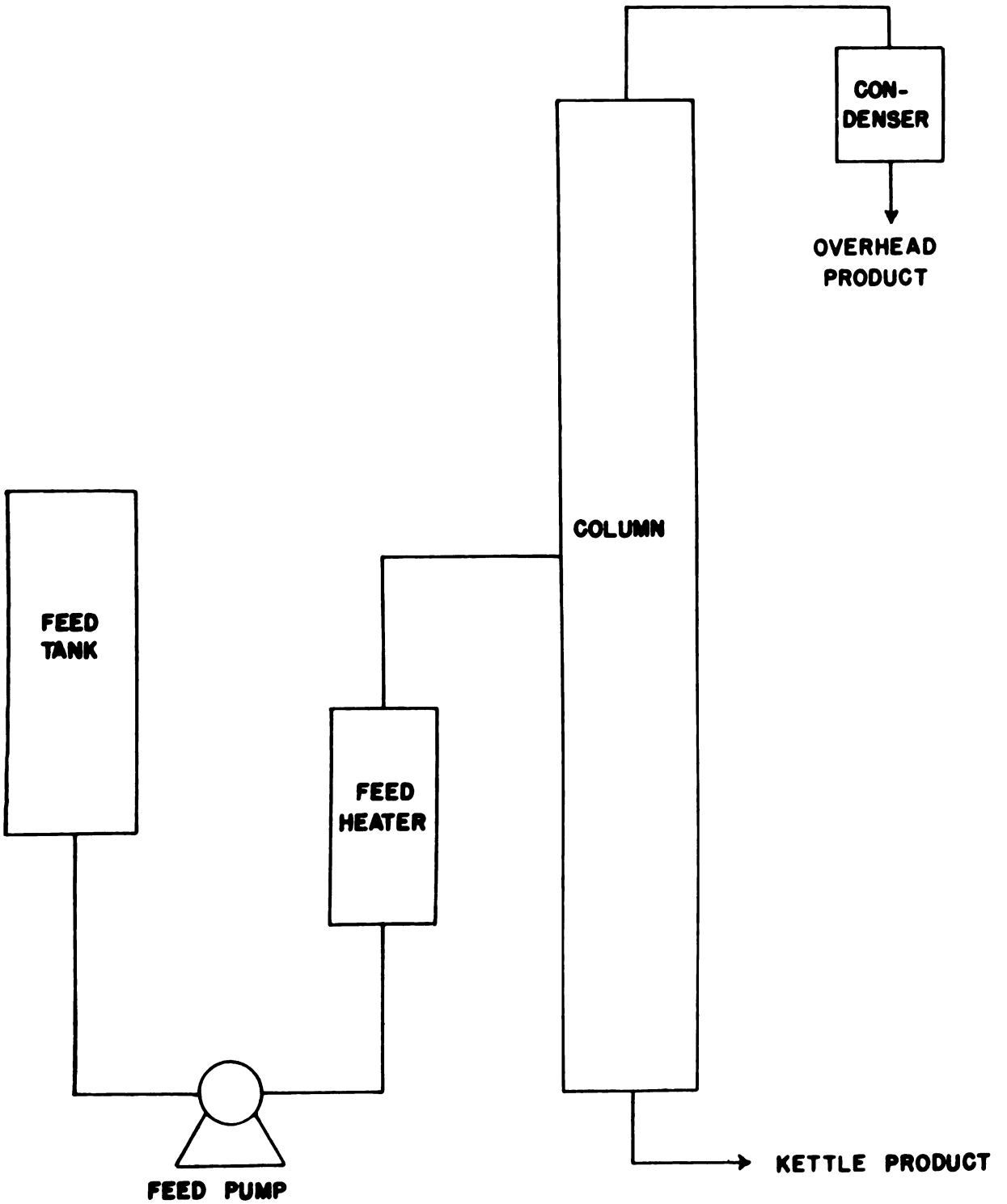

Figure 9. - Continuous distillation unit flow sheet.

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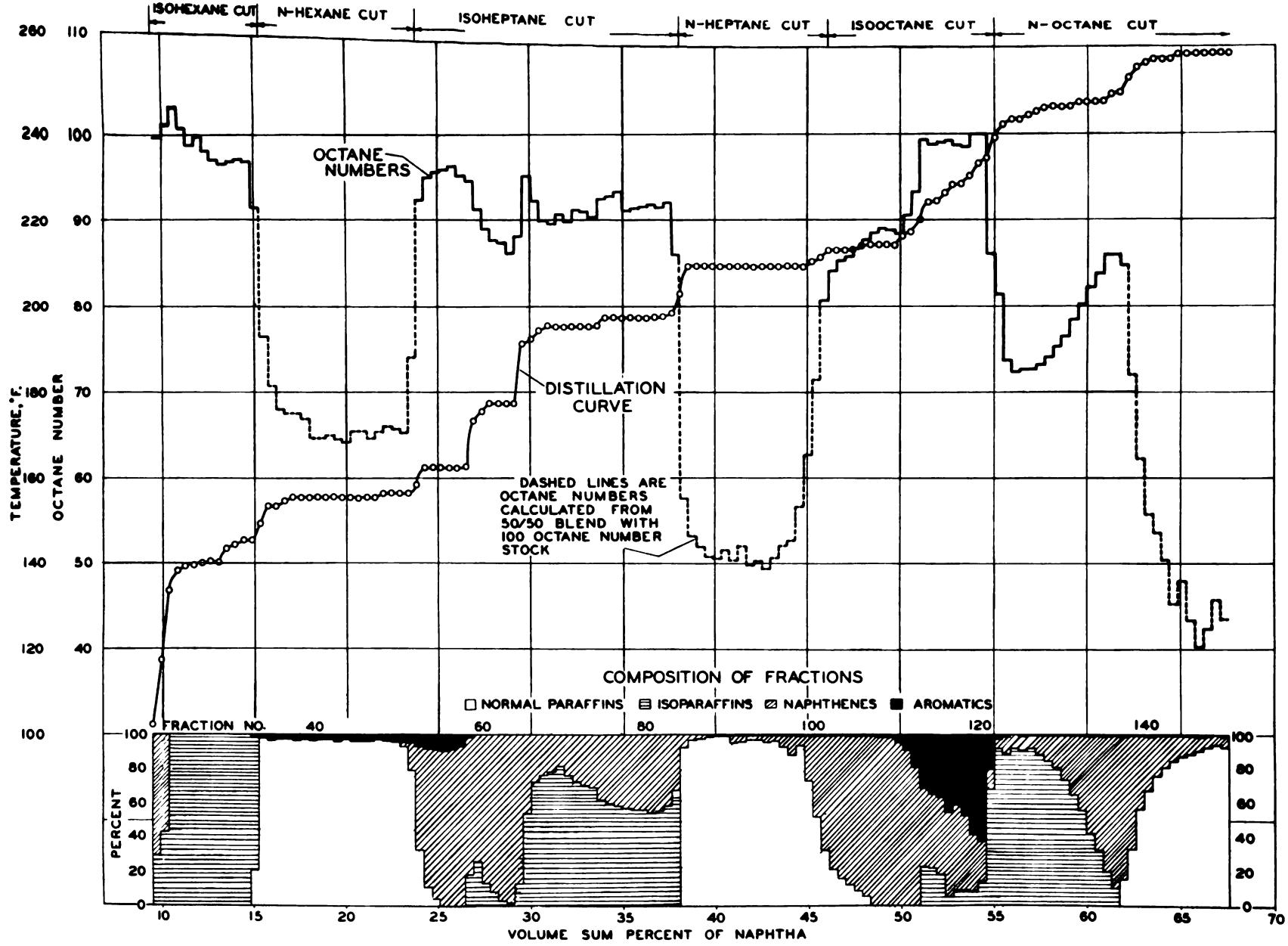

Figure 10. - Curves showing relationship of octane number to composition and distillation temperature.

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information. Therefore, the Bureau not only collects its crude-oil samples in the field wherever possible, but it also distills enough of a desired product (sometimes several hundred gallons) to carry out all of the subsequent tests. Figure 9 shows the essential parts of a "continuous" still that is well-adapted to the needs of the current program. A desirable feature is that so long as the charging rate, the temperature, and the product-withdrawal rate are maintained constant, material can be charged indefinitely, and the same product can be produced continuously.

A continuous topping unit of 5-gallons-per-hour capacity was designed, and its construction is about 50 percent complete. This unit will be used to separate the crude oil into two major fractions. The product or overhead fraction, boiling up to 300°F., will be studied to determine its suitability as high octane-number aviation-gasoline base stock. The residual fraction will be processed further to obtain material boiling in the 300°-700° F. range for study as a source of gas-turbo and Diesel fuels.

Superfractionation Studies

Superfractionation, which, in contrast with continuous distillation, is a batch process, permits the collection of a series of small fractions each having a very narrow boiling range. The series as a whole may cover a wide boiling range. This method was used to obtain very effective fractionation of naphthas in the 100°-300°F. range in the Bureau's war research to find aviation-base stocks suitable for use in the preparation of 115/145 performance number aviation fuels. This type of work is so important that it is being continued as a part of the present program.

During the year, naphthas from Oklahoma City, Okla., crude oil 27/ and Santa Barbara, Venezuela, crude oil were superfractionated, and 0.5 percent fractions were collected. Each fraction was analyzed for composition in terms of individual hydrocarbons by the hydrocarbon-analysis group, and the fuel-combustion group determined its engine rating (octane number) with 4.0 ml. tetraethyllead by the CRC-F-3 (lean mixture) method. (A discussion of engine-testing methods is given under the section on fuel combustion). All of these data for the Oklahoma City oil are brought together in figure 10. The overhead temperatures (distillation curve) and the octane numbers of the individual fractions have been plotted against volume sum-percent distilled. At the bottom of this chart is a bar-graph that gives the composition of each fraction in terms of normal paraffins, isoparaffins, naphthenes, and aromatics to indicate relationships between octane number and composition.

27/ Petroleum Chemistry and Refining Staff, War Research Report on Aviation Gasoline and Component Hydrocarbons, Preparation of 115/145 Grade Aviation Fuel Using Base Stock Made by Superfractionation of Naphtha from Oklahoma City, Okla., Crude Oil, PCR 45-006: Petroleum Experimental Station, Bartlesville, Okla., December 1945, 26 pp.

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Fractions rating higher than 84 octane number were combined as indicated to give "isohexane", "isoheptane", and "isoctane" cuts. These iso-cuts were blended individually with high-octane blending agents to prepare 115/145 grade aviation fuel. The composition and octane numbers of the fractions were used to calculate the octane numbers of the individual hydrocarbons blended with the hydrocarbons with which they normally are associated (see section on fuel combustion). The octane numbers of 13 naphthas in the boiling range 97°-243°F. were calculated, using these blending values and the composition as determined by laboratory superfractionations and analyses of the fractions by specific dispersion and refractivity intercept methods. (These analyses were made and reported during the war in conjunction with studies on aviation base stocks.) The maximum difference between the calculated and determined octane number for these 13 naphthas was ±3 octane numbers. Some of the data obtained in the study of Oklahoma City naphtha were contained in a paper presented before the Division of Petroleum Chemistry of the American Chemical Society in Atlantic City, N. J.,28/ and this paper has been submitted to Industrial and Engineering Chemistry for publication.

Continuation of superfractionation studies applied to fuel oils in the 300°-700° F. boiling range will necessitate a high-vacuum distillation unit, and plans for such equipment are being developed.

Batch Distillation of Crude Oils and Their Products

Early in 1945, the National Advisory Committee for Aeronautics requested the Bureau of Mines to make a survey of the availability of fuels for jet-propulsion or gas-turbo engines. For this work, 5-liter batch distillations were made of 10 selected crude oils, followed by analyses of the fractions. These distillations were so conducted that the fractions were virtually identical in volume percentages and specific gravities with those of Bureau of Mines Hempel distillations of the same crude oils. After the properties of the many fractions were determined, it was possible to develop correlations between Bureau of Mines Hempel analyses of crude oils and Army-Navy specifications for jet-propulsion fuels. This made possible the classification of crude oils as sources for such fuels by the use of routine analytical data alone. The oils from 30 major fields, each producing more than 25,000 barrels per day, were classified as to their suitability as sources of jet-propulsion fuel. Thirteen fields were suitable, 13 fields were unsuitable, and 4 fields were doubtful. This work29/ was reported in October 1945 and is of value, aside from the jet-propulsion fuel

28/ Ward, C. C., Gooding, R. M., and Eccleston, B. H., Superfractionation Studies: Composition and Octane Numbers of 0.5 Percent Fractions of an Oklahoma City Naphtha: American Chemical Society, Atlantic City, April 1946.

29/ Petroleum Chemistry and Refining Section, Report on Possible Crude-Oil Sources for Jet-Propulsion Fuels: Petroleum Experiment Station, Bartlesville, Okla., October 1945. Restricted.

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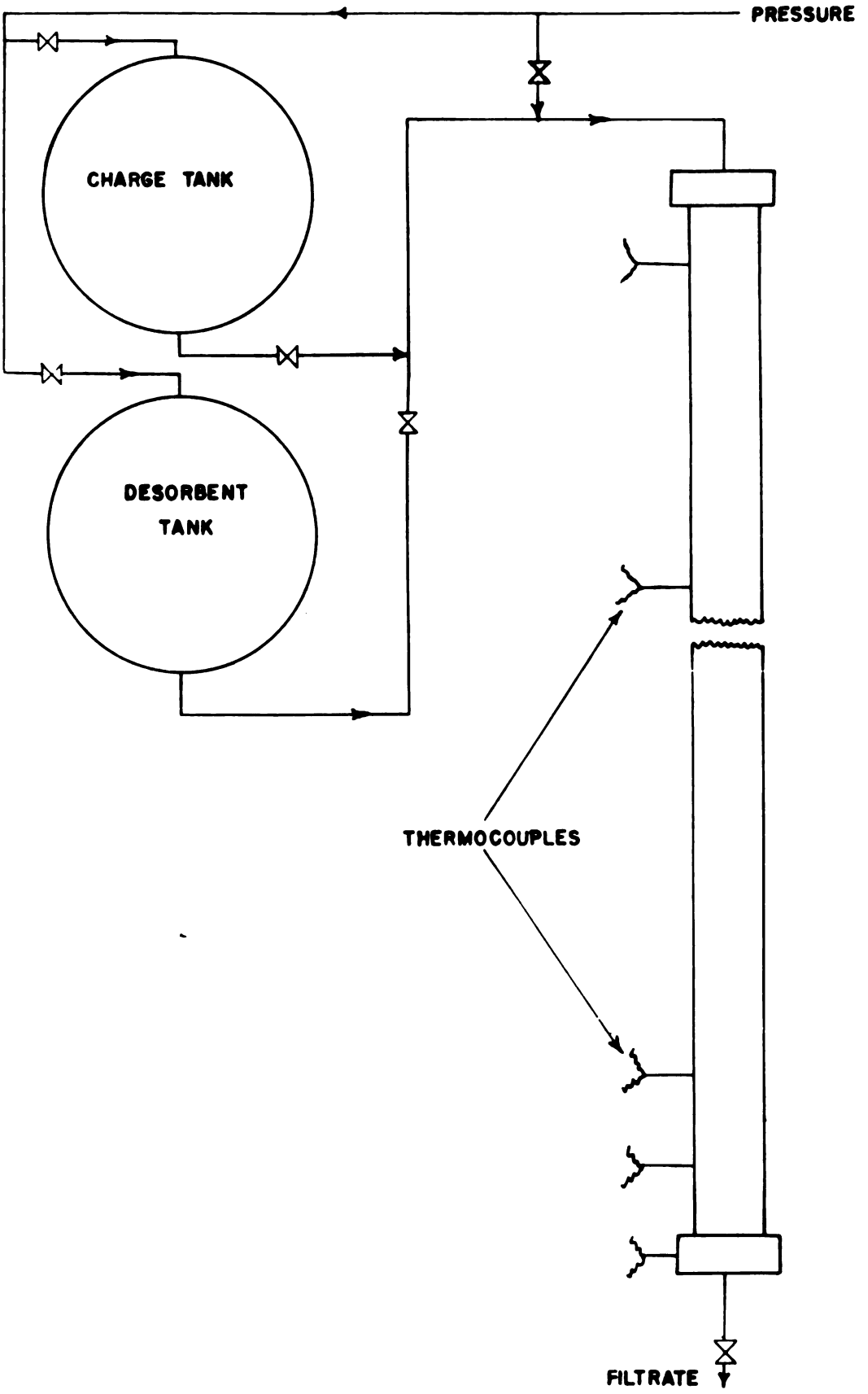

Figure 11. - Pilot plant silica gel adsorption column.

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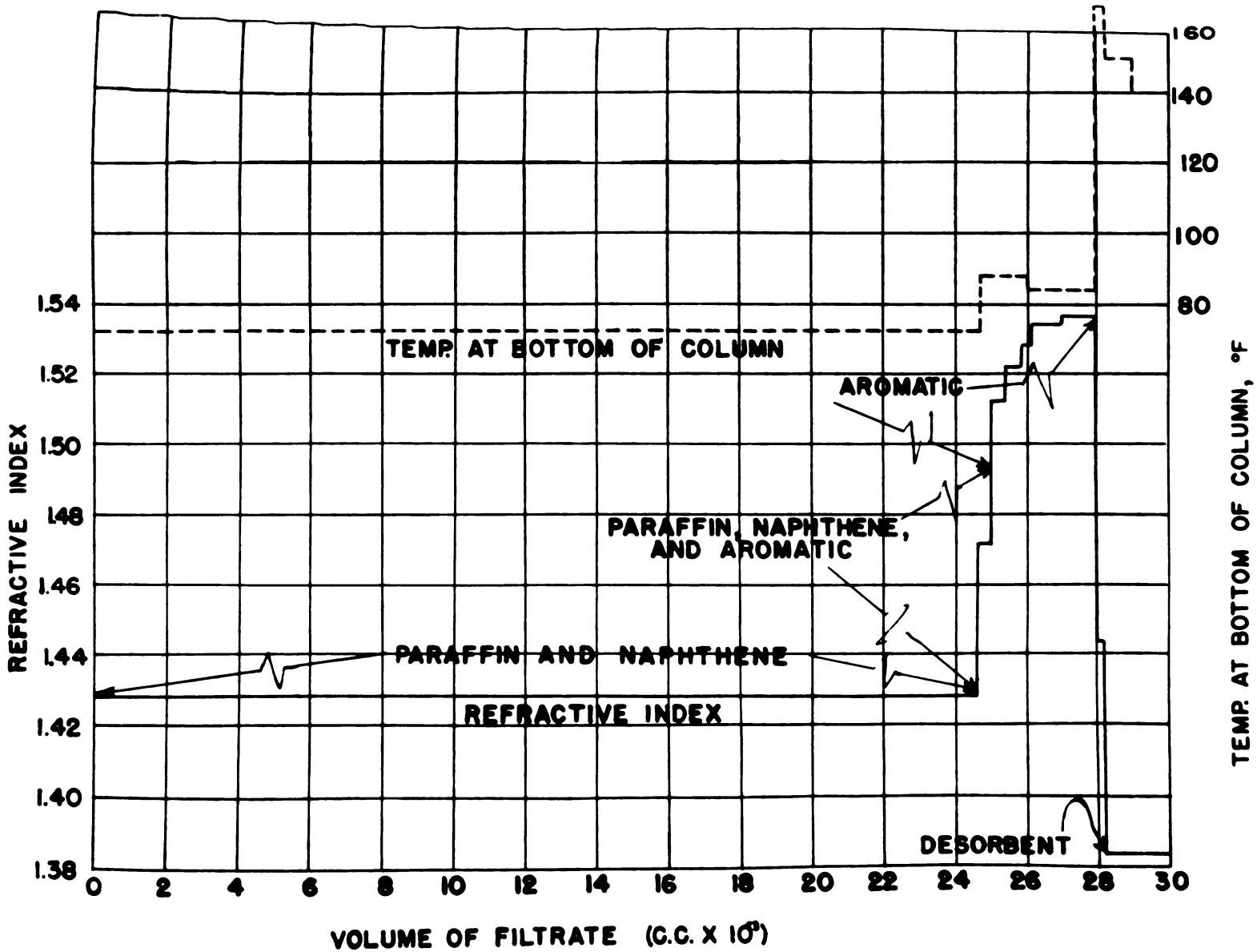

Figure 12. - Silica gel adsorption curves.

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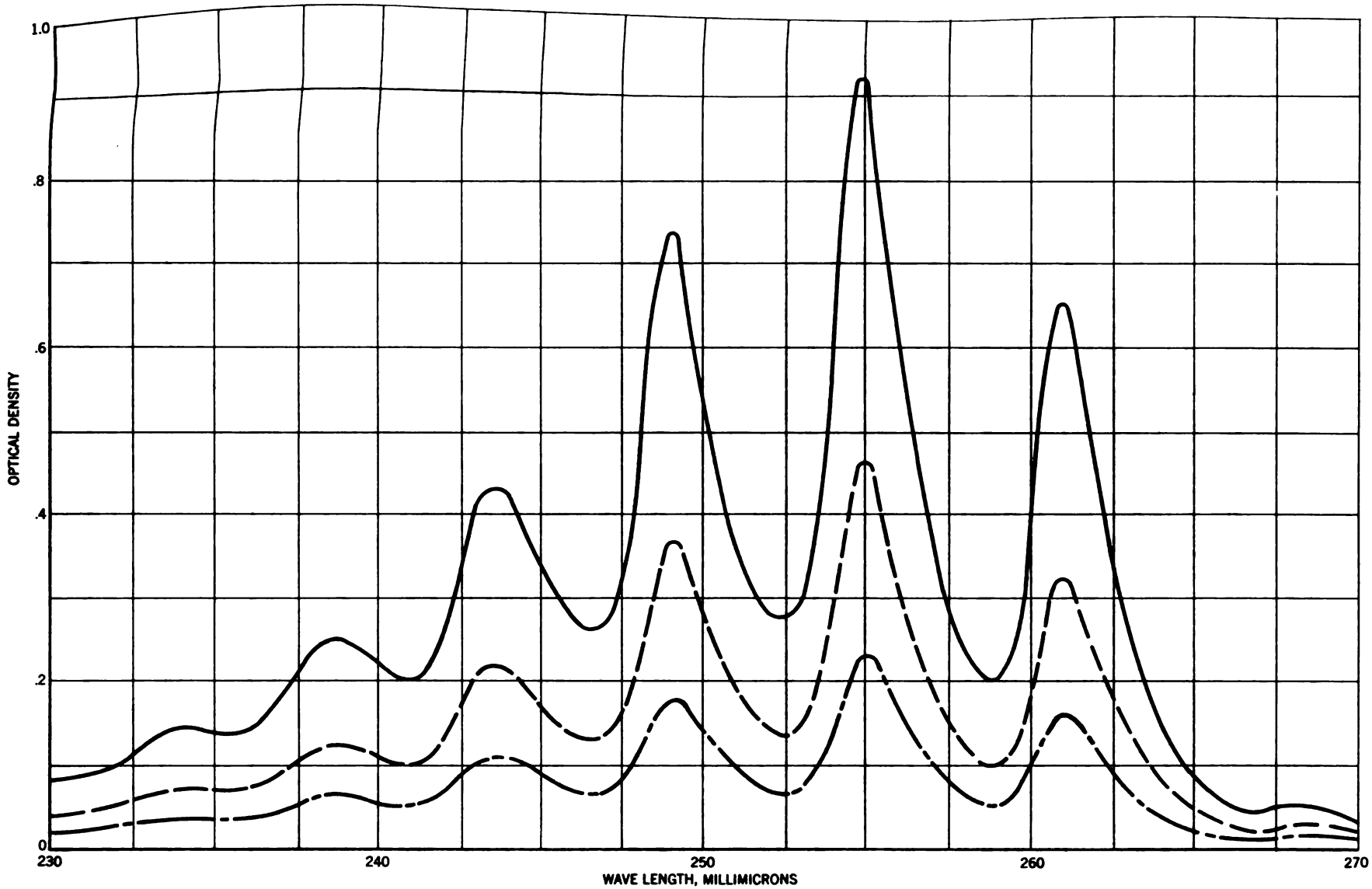

Figure 13. - Typical absorption curves of samples containing benzene.

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consideration, because of the tabulation listing determined and calculated properties for a series of narrow-boiling fractions from every major type of crude oil produced in the United States. (See fig. 13)

Silica Gel Adsorption of Naphthas and Fuel Oils

All petroleum fuels consist of essentially paraffins, naphthenes, and aromatic hydrocarbons, differing for the most part only in the relative proportions. Distillation, even superfractionation, will not completely separate these types, and recourse must be made to other means if actual physical separation is desired. The removal of aromatic compounds is especially desirable for several reasons: (1) To avoid the formation of aromatic azeotropes in analytical distillation; (2) to improve the ignition and combustion qualities of Diesel fuel and jet-propulsion fuels, respectively; and (3) to remove traces of aromatics from pure hydrocarbons. Such segregation of aromatics can be accomplished by filtration through silica gel under suitable conditions.

A silica-gel adsorption column 3 inches in diameter and 21 feet long, of stainless steel, was designed and constructed (fig. 11). The process used is essentially the same as that in small-scale laboratory experiments (described later under hydrocarbon analyses). Typical data for a silica gel adsorption are shown in figure 12, in which the refractive index of the filtrate is plotted against its volume. The sharp break between paraffins plus naphthenes (low refractive index) and aromatics (high refractive index) illustrates the quantitative separation possible by the use of silica gel adsorption. The course of the adsorption can be followed easily by the heat changes that occur at the various adsorption boundaries. These temperatures are shown in figure 12 by a dash line. Typical results are shown in the following table.

TABLE 3. - Separation of paraffins plus naphthenes from aromatics

Fraction	Refractive index	Hydrocarbon type	Filtrate	
			Ml.	Percent
1	1.4290	Paraffin-naphthene	24,950	88.2
2	1.4448	Paraffin-naphthene-aromatic	100	0.3
3	1.4725	do.	100	0.3
4	1.4885	do.	100	0.3
5	1.4993-1.5345	Aromatic	2,000	7.1
6	1.5350	do.	950	3.4
7	1.4489	do.	100	0.3
8	1.3850	Aromatic desorbent	50	0.1

Desulfurization of Naphthas, Fuel Oils, and Crude Oils

The production of suitable petroleum products from "high-sulfur" or so-called "sour" crude oils has been a troublesome problem for refiners for many years. Many of the high-sulfur oils are capable of yielding products whose components, exclusive of the sulfur compounds, are such as to make these products highly satisfactory for various uses. During

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the past few years, several processes utilizing catalysts have been developed for satisfactory desulfurization of light distillates. One of this general class is the "hot-earth" (bauxite) catalytic desulfurization process, wherein all the sulfur compounds (with the exception of cyclic compounds) usually found in virgin distillates are decomposed, the sulfur being converted to hydrogen sulfide. This decomposition is accomplished by vaporizing the distillate, superheating the vapors to 700° F., and passing them through bauxite at a relatively low pressure. Frequently, after the condensed vapors are washed with caustic to remove hydrogen sulfide, virtually sulfur-free distillate is obtained.

The favorable results from using this process for the beneficiation of aviation base stock 30/ led to experiments in which this catalyst was used directly with crude oil. These showed that bauxite-treating not only reduced the sulfur content but also increased the percentage of light hydrocarbons at the expense of residual material. To determine the extent of desulfurization and conversion attainable, a series of experiments was outlined and carried out at 750° F. with a liquid space velocity of one volume of charge per hour per three volumes of catalyst. Crude oil in volumes of 1, 3, 5, and 6 liters was processed over 2,400 ml. of new catalyst. A steam purge was used to minimize the amount of oil held on the catalyst.

The desulfurized crude-oil samples were subjected to Bureau of Mines Hempel distillations, sulfur determinations, and fractional and vacuum distillations. Further sulfur determinations were made on the gasoline, gas oil, and residual fractions. Analyses of gasoline fractions by silica gel adsorption and superfractionation and determination of the octane numbers of the gasoline fractions are being made; analyses of catalyst samples for oil, carbon, and sulfur deposits were completed.

Table 4, based on data from Hempel analyses, shows a comparison of the properties of the original crude oil and those of crude oil treated in the ratio of one liter of crude oil to 2,400 ml. of new bauxite. A Report of Investigations is now in preparation on the desulfurization of crude oil in a bauxite catalyst.

TABLE 4. - Comparisons of original and desulfurized Slaughter crude oil

	Original	Desulfurized
Specific gravity	0.863	0.820
A.P.I.° gravity	32.5	41.1
Sulfur, percent	2.06	0.71
Saybolt Universal viscosity at 100° F.	26 sec.	32 sec.
Color	Greenish-black	N.P.A. No. 4
Carbon residue of residuum	14.3	2.4
Carbon residue of crude	3.9	0.1

30/ Guthrie, Boyd, and Simmons, M. C., Effects of Desulfurization upon the Lead Susceptibility of Distillates from Some Crude Oil from Texas, New Mexico, and Oklahoma: Bureau of Mines Rept. of Investigations 3729, 1943, 16 pp.

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Approximate Summary

	Percent	Sp. gr.	Percent	Sp. gr.
Light gasoline	11.0	0.706	14.7	0.711
Total gasoline and naphtha	31.4	.754	46.3	.759
Kerosine distillate	4.4	.813	6.9	.820
Gas oil	18.6	.857	27.5	.864
Nonviscous lubricating distillate	8.35	.897-.914	9.9	.892-.911
Medium lubricating distillate	7.25	.914-.928	4.4	.911-.923
Viscous lubricating distillate	.7	.928-.929	-	-
Residuum	27.3	.911	4.2	.960
Distillation loss	2.0		.8	

Hydrocarbon Properties and Analyses

Synthesis and Purification of Hydrocarbons

In petroleum research, pure hydrocarbons are required as laboratory reference standards for the synthesis of blends of hydrocarbons and for determining physical and chemical properties. At present, the literature is scattered widely, and the Bureau has found it highly advantageous to prepare abstracts of articles on the synthesis of saturated and aromatic hydrocarbons in the boiling range 160°-350° C. and on their principal physical properties (density, boiling point, and refractive index.)

In the laboratory, five compounds of the diphenyl series of aromatics, not available commercially, were synthesized and subjected to preliminary purification. The five are diphenylmethane, 1,1-diphenylethane, 1,2-diphenylethane, 1,3-diphenylpropane, and 2,2-diphenylpropane. Intermediates in the synthesis of two other compounds in this series were prepared.

The hydrocarbons 2,2,4-trimethylpentane (iso-octane), methylcyclohexane, and toluene were prepared in 4-liter quantities as secondary reference standards for calibrating density balances and refractometers and for blending purposes.

One-liter samples of 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and methylcyclohexane were purified for the determination of thermodynamic data. Some 18 to 20 additional hydrocarbons were purchased or synthesized and await further purification in lots of 1 to 20 liters.

Properties of Hydrocarbons

At least 10,000 determinations of individual physical properties of hydrocarbons or mixtures of hydrocarbons were made during the year. These included refractive indices at five wave-lengths of light, densities at several temperatures, viscosities at several temperatures, boiling points at several pressures, freezing points, and aniline points; also, many calculated properties derived from these data, such as specific dispersions - the difference between the refractive indices at two wave-lengths of light, divided by the density. Most of the determinations, however, were refractive-index and density measurements such as were used in analyzing the fractions

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of Oklahoma City naphtha (see footnotes 27 and 28) and in the studies of jet-propulsion fuels (see footnote 29).

Development of Spectrometric Analytical Methods

Whenever radiant energy traverses any transparent homogeneous material, a portion of the incident energy is absorbed by the material. This absorption is measured by comparing the intensity of the radiation impinging on the medium to that after its emergence from the medium. For monochromatic radiation, the logarithm of this ratio (optical density) is directly proportional to the thickness of the medium traversed and (in the case of solutions) to the concentration of the "absorber" in a solution of a "nonabsorber" - that is, a material in which the absorption is small in comparison with that of the "absorber." These measurements may be made with an instrument called a spectrometer. Because of practical considerations, special instruments are required for investigations in specific ranges of radiation. Thus, the ultraviolet spectrophotometer is employed in the range 200 millimicrons to about 2,000 millimicrons, which covers the near ultraviolet, visible, and a very small portion of the near infra-red radiation. The infra-red spectrometer is used principally in the range 1,000 millimicrons to 25 microns. With these instruments and with proper technique and calibration, it is possible to make unique investigations leading to information, obtainable in a few minutes, which would be almost impossible, and certainly time-consuming, to obtain by other physical or chemical methods. Thus, for example, with such equipment it is possible to measure quantitatively the concentration of certain materials in solutions, to recognize and estimate the quantity of an impurity in compounds of high purity, and to measure the rates of chemical reactions. On the qualitative side, these instruments can verify the gross structure of unknown molecules or identify specific molecular groupings or bonds and thus aid in establishing the presence of or final identification of unknown molecules.

Figure 13 illustrates how such instruments are used. This figure is a graph of the optical density as a function of the wave lengths of monochromatic light in the ultraviolet region for benzene in isooctane at two concentrations (solid lines). A sample containing an unknown quantity of benzene is shown by a dash line. If the instrument has been calibrated in terms of known quantities of benzene, then it is possible to determine accurately the benzene content of the sample by relatively simple calculations based on relationships between optical density and concentration for the several solutions.

The Bureau's staff has found extensive use for these optical analytical methods and, to advance the research, has made a study of the literature on ultraviolet absorption spectra for aromatic hydrocarbons boiling below 350° C.

The ultraviolet spectrophotometer was used recently for the estimation of aromatics present in petroleum fractions from distillation and chromatographic columns. It was used extensively, also, in cooperative work with Sub-committee XXV-F of Committee D-2, A.S.T.M., in standardizing methods

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and procedures for estimating benzene and toluene in petroleum distillates and commercial products. It is anticipated that this instrument will find use in the estimation of aromatic hydrocarbons in the entire 100°-700° F. boiling range. The infra-red spectrometer, not yet completely installed, will be especially useful in resolving analytical problems involving paraffin and naphthene hydrocarbons.

Development of Non-Optical Analytical Methods

The Bureau of Mines has been analyzing various virgin naphthas and condensates since early in 1942 to determine their possibilities as sources of aviation-gasoline base stocks, toluene, and other hydrocarbons. These analyses are based essentially upon fractional distillation of the naphthas or condensates and refractometric examination of the distilled fractions. The final data obtained from such analyses indicate the quantities of aromatics, naphthenes, and paraffins in the sample boiling below 320° F. The quantities of most individual hydrocarbons boiling below 243° F. can be determined. A report 31/ describing the method was published recently.

A supplement of this work has been the cooperative development, with Subcommittee XXV of A.S.T.M. Committee D-2, of analytical methods for gasoline without using fractionation.

Particular emphasis was given to the improvement of A.S.T.M. Method ES-45a for the determination of aromatics and olefins in gasolines, 32/ the standardization of an apparatus for determining freezing points and purities of purified hydrocarbons, and improvement and standardization of methods for refractive-index and density measurements.

Petroleum products frequently require analysis and physical separation into hydrocarbon types and individual hydrocarbons. Filtration of distillates through silica gel offers a convenient and rapid method for separating aromatic compounds from their mixtures with paraffins and naphthenes and for the estimation of aromatic contents. The sample to be analyzed is introduced into the top of a column containing silica gel. When all the sample has entered, ethyl or isopropyl alchohol is added. The alcohol desorbs the hydrocarbons from the gel and forces them down the column. In this process the hydrocarbons are fractionated according to their adsorbability. The components issue from the column in the order: paraffins plus naphthenes, aromatics, alchohol. The filtrate is collected in appropriate small measured fractions whose refractive indices are determined. From a graph (see fig. 12) of the refractive indices of the filtrate fraction, the volume percentage of (a) the aromatics and (b) the naphthenes plus paraffins may be determined.

31/ Gooding, R. M., Adams, N. G., and Hall, H. T., Determination of Aromatics, Naphthenes, and Paraffins by Refractometric Methods: Ind. Eng. Chem., anal. ed., vol. 18, Jan. 15, 1946, p. 2.

32/ A.S.T.M. Standards on Petroleum Products and Lubricants, p. 486, Sept. 1945; Emergency Method of Test for Olefins, Aromatics, Paraffins and Naphthenes in Aviation Gasoline (Without Distillation into Fractions): A.S.T.M. Designation ES-45a.

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The use of adsorbents is still in the developmental stage, and during the year studies were made of the specific action of various adsorbents, such as alumina and charcoal, and also of several desorbents. Silica gel adsorption as an analytical method for the determination of aromatics in petroleum distillates was extended to included a method for determining naphthalene aromatics in these samples. This method33/ will be presented to the American Chemical Society meeting in Chicago during September 1946.

An apparatus for the determination of hydrogen in liquid organic compounds was modified and improved so that carbon dioxide and, hence, carbon also could be determined quantitatively. The type of lamp used with the modified apparatus has a provision for introduction of purified air below the top of the wick, making it possible to burn aromatic hydrocarbons with a smoke-free flame. octane, toluene, and isopentane were burned successfully in the lamp, and carbon-hydrogen ratios were obtained for these pure compounds. The maximum deviation for repeated analyses from the mean is about 0.01 percent when 0.5 to 1.0-gram samples are used. Figure 14 shows the modified apparatus used in the carbon and hydrogen determinations. A paper34/ describing this method has been submitted to the Analytical Edition of Industrial and Engineering Chemistry for publication.

Application of Analytical Methods to Naphthas Fuel Oils, and Crude Oils

The most extensive application of analytical methods during the year was the study of the fractions from the 10 selected crude oils reported in the investigation of jet-propulsion fuel sources. (See footnote 29.) This work included silica-gel adsorption analyses for aromatic and naphthalene contents, viscosity measurements, and determinations of freezing points and other related properties of 150 or more similar naphtha fractions. Additional work along similar lines included the analysis of 11 jet-fuel stocks procured from the National Advisory Committee for Aeronautics laboratory at Cleveland, Ohio, and of three stocks supplied by the Army Air Forces at Wright Field, Dayton, Ohio.

The type and extent of this work is indicated in figure 15, where the composition of the several fractions from the 10 crude oils is shown in terms of paraffins, mono- and dicyclic naphthenes, and mono- and dicyclic aromatics. The fraction numbers represent a boiling-point range from an initial of about 80° F. for fraction 2 to an end-point of about 600° F. for fraction 10.

A total of 25 gas samples, including four from fields in the State of Bahia, Brazil, were analyzed by low-temperature fractional distillation, and 37 Orsat analyses were completed. Most of these analyses were made in conjunction with the crude oil-desulfurization studies previously discussed.

33/ Gooding, R. M., and Hopkins, R. L., The Determination of Aromatics in Petroleum Distillates.

34/ Simmons, M. C., A Lamp Method for the Determination of Carbon and Hydrogen in Petroleum Distillates.

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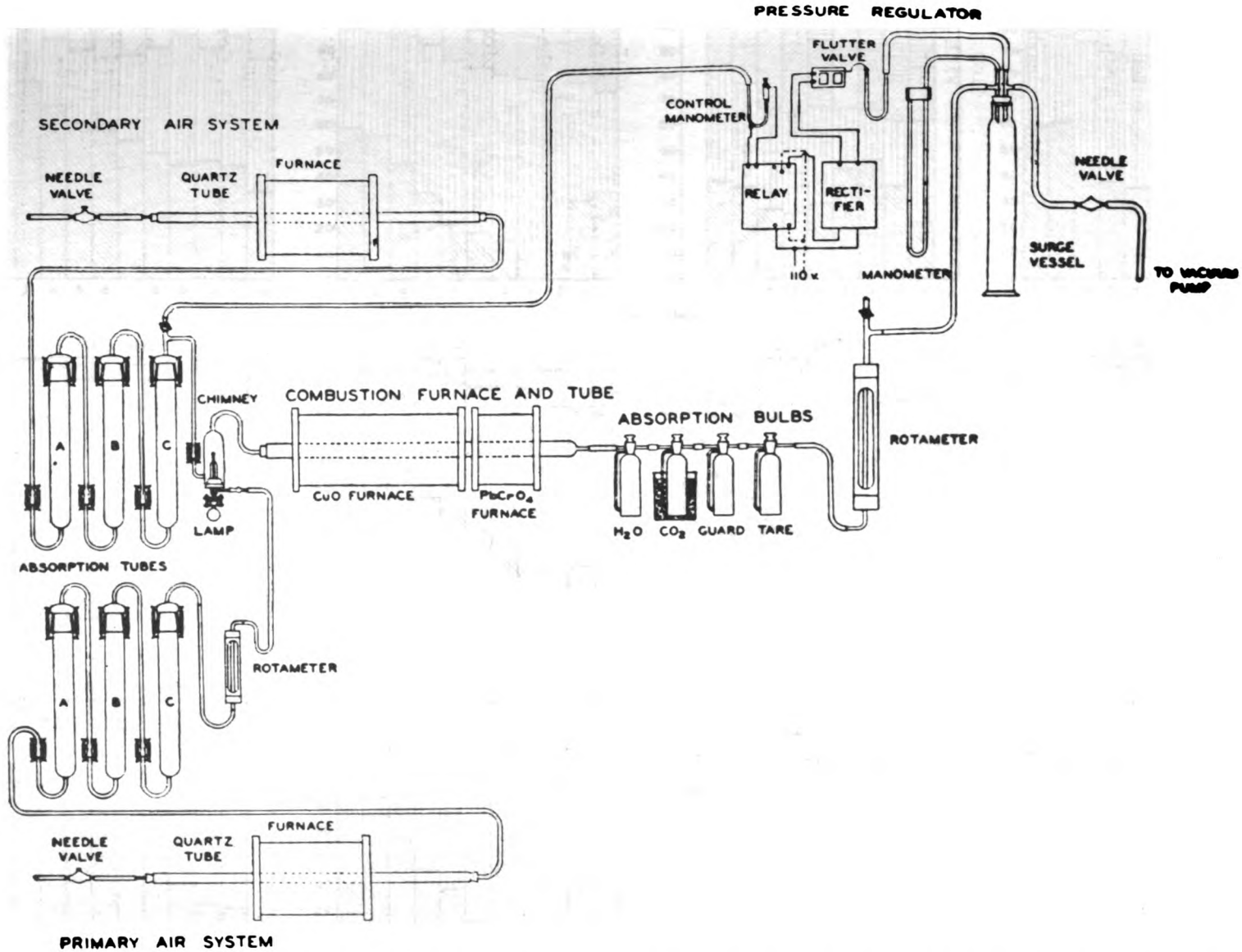

Figure 14. - Diagram of apparatus for simultaneous determination of carbon and hydrogen.

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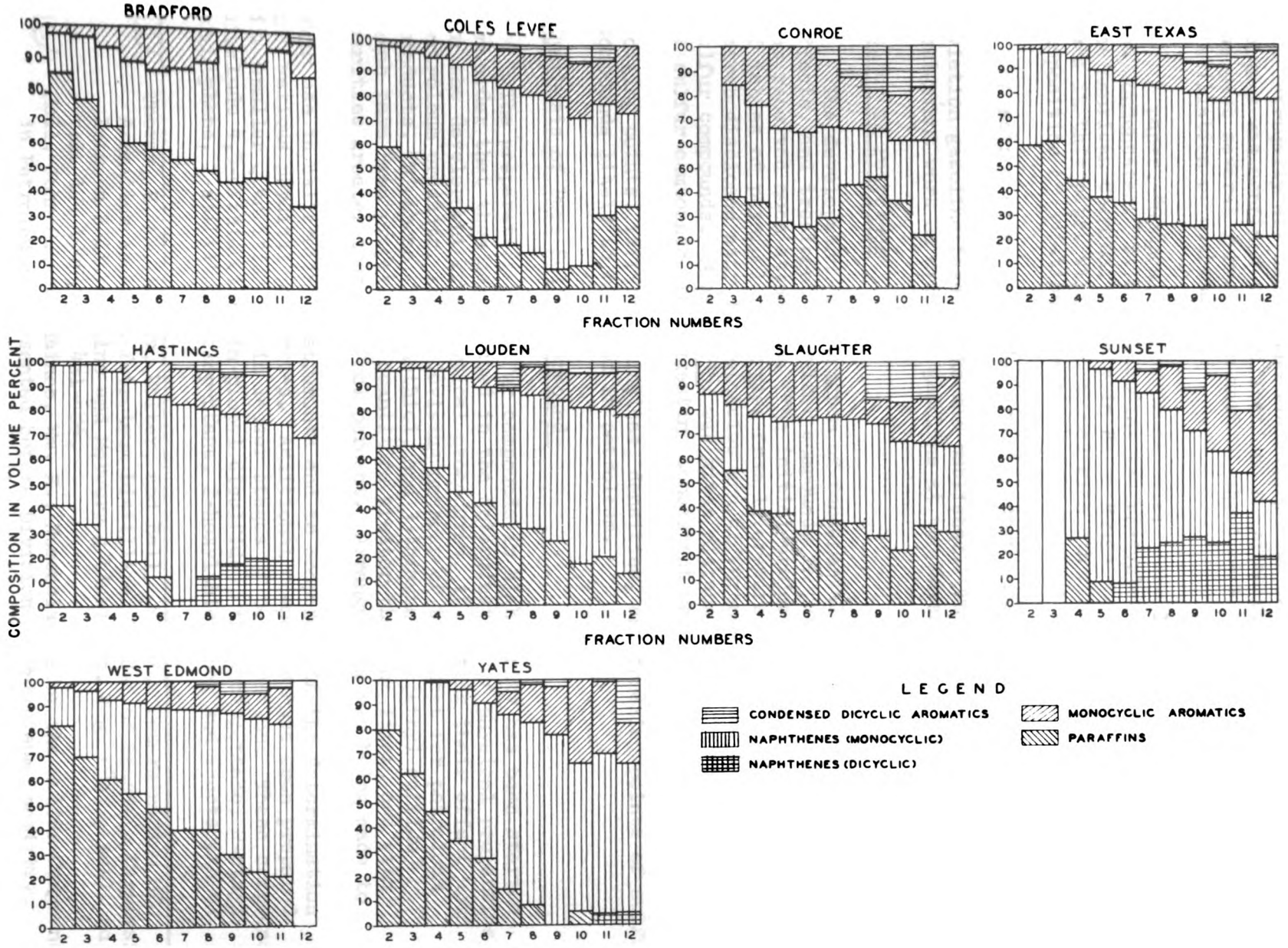

Figure 15. - Composition of fractions from typical crude oils.

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Virtually all use of the laboratory high-temperature distillation columns was confined to purification of hydrocarbons in contrast to work of the past several years, when most of the time was devoted to the analytical distillation of naphthas.

A paper, "Composition of Crude Oils: Some Texas and Louisiana Naphthas and Condensates," by R. M. Gooding was presented to a regional meeting of the American Chemical Society in Baton Rouge, La., in October 1945. The data in this paper will be combined with other data to form a paper on the composition of aviation base stock from various sources.

A method of analysis for aromatic compounds35/ that was developed for use in the evaluation of crude oils as sources for toluene, benzene, and aviation gasoline base stocks was published. This completed the war assignment work on aviation gasoline at the Laramie Station.

Sulfur in Petroleum

The development of a program of fundamental research on the properties, effects, and treatment of sulfur compounds in petroleum and its products has received much attention. The initial project has been the compilation of tables of physical properties from literature sources. This literature search disclosed many discrepancies and differences in the naming of the sulfur compounds. A report36/ was given discussing usages in the nomenclature of sulfur compounds and suggesting consistent methods of naming. A report is in preparation summarizing the data obtained from the literature on boiling points, refractive indices, densities, and freezing points of sulfur compounds likely to be found in petroleum.

Synthesis of Pure Sulfur Compounds

The preparation of sulfur compounds in high purity has been started in order that they may be used in the determination of physical properties, in the development of analytical procedures, in testing their effect upon petroleum products, and in devising methods of treatment for petroleum products. Thiophene, pentanethiol, and 3-thiapentane (ethyl sulfide) each have been prepared in quantities greater than one liter, and with purities greater than 99.5 mol percent. Arrangements are being made to permit release of portions of the purified compounds to other laboratories for use in calibrating instruments and to cooperate in the determination of various physical properties. Additional compounds have been prepared in smaller quantities and in lesser stages of purification. These compounds include 4,5-dithiaoctane (n-propyl disulfide), thiacyclopentane, 2-ethylthiophene, 2-methylthiacyclopentane, 2-hexylthiophene, and 2-octanethiol.

35/ Thorne, H. M., Murphy, Walter, and Ball, John S., Determination of Aromatics in Light Petroleum Distillates by Use of Specific Dispersions Between Sodium D Line and Mercury g Line: Ind. Eng. Chem., anal. ed., vol. 17, 1945, pp. 481-486.

36/ Ball, John S., and Haines, Wm. E., Nomenclature of the Sulfur Compounds in Petroleum: Presented before Division of Petroleum Chemistry, American Chemical Society, Atlantic City, N. J., April 10, 1946.

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Fuel Combustion in Engines

The investigations of Diesel fuels, of internal combustion spark-ignition fuels, and of fuel desulfurization all have as their objective improved utilization of fuels in engines. Thus far, technological developments have not progressed to the point where engine performance can be predetermined from analytical and inspection data on the fuel, and final indication of expected performance is still obtained by actual combustion in test engines. It is necessary, therefore, to carry on combustion research in conventionalized test engines to supplement and complement the property and composition data concurrently obtained on various types of fuels.

The most important property of a fuel intended for use in an internal-combustion, spark-ignition engine is its detonation characteristic or octane number. This property is evaluated by means of standard single-cylinder test engines of variable compression ratio, wherein the test fuel is compared as to knock characteristics directly with known reference fuels. However, it has been shown, through years of research, that the performance of a fuel in any one engine is not a criterion of the performance of that fuel in all types of internal-combustion engines. In an attempt to predict the performance of fuels in different types of engines, five laboratory test methods have been approved by the Coordinating Research Council, Inc.

The engine laboratory at the Bartlesville station is equipped to test motor fuels by one method (CRC-F-2) and aviation fuels by two methods (CRC-F-3 and CRC-F-4). The method of test for knock characteristics of motor fuels (F-2) has been accepted as standard by the American Society for Testing Materials (A.S.T.M.) and designated D375-45. The method of test for aviation fuels (F-3) has been adopted by A.S.T.M. as a tentative standard and designated D614-44T. The two methods utilize essentially the same equipment but differ in instrumentation and in the temperature at which the engines are operated. The following tabulation compares the two methods:

CRC designation	F-2	F-3
ASTM designation	D375-45	D614-44T
Method	Motor	Aviation (Lean
Engine speed	900 ± 9	1200 ± 12
Spark advance	Automatically varied with compression ratio 26° at 5.1	Fixed at 35° ± 1
Oil pressure	25-30 psi SAE 30 oil	60 ± 10 psi SAE 40 oil
Oil temperature	120-150° F.	150° ± 10° F.
Jacket temperature	209°-215° ± 1° F.	374° ± 9° F.
Humidity	25-50 grains per lb. air	25-50 grains per lb. air
Intake air temperature	75°-125° F.	125° ± 5° F.
Mixture temperature	300° ± 2° F.	220° ± 2° F.
Carburetor adjustment	Maximum knock	Maximum temperature
Knock intensity	Standard knock intensity given by guide tables of compression ratio or micrometer setting as octane number	Adjusted so that cp. benzene is equal in thermal plug temperature to 87.0 octane reference fuel
Instrumentation	Bouncing pin	Thermal plug

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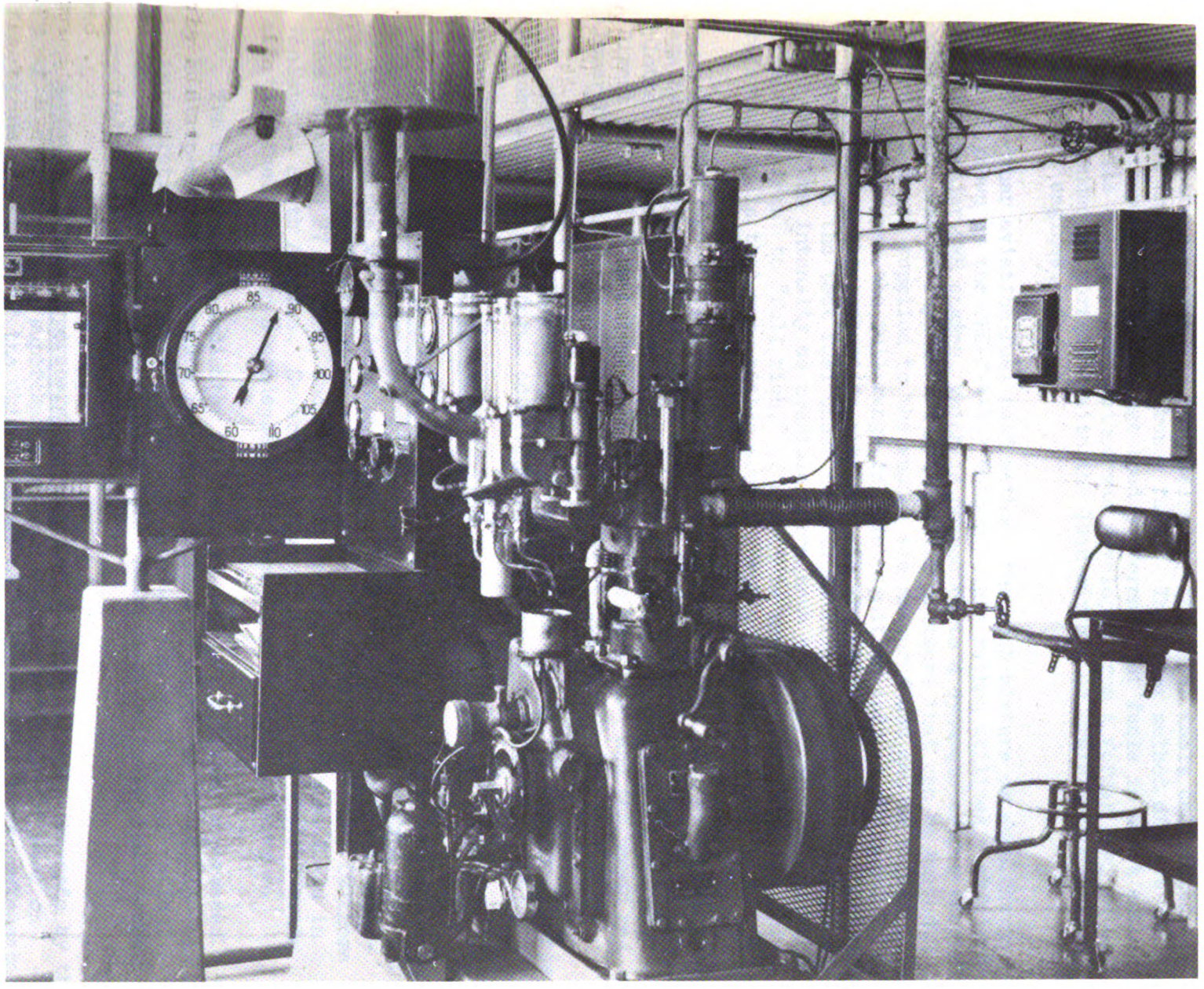

Figure 16. - ASTM-CFR fuel-research unit for determining lean-mixture knock characteristics of aviation fuels.

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In both the above methods, the test fuel is compared directly with a blend of isooctane in n-heptane (percent isooctane in normal heptane is defined as octane number) or with secondary reference fuels calibrated in terms of these primary reference fuels. The motor method of test was developed to predict the average road performance of fuels in stock automobiles. The aviation lean method was developed from a former Army method and is intended to correlate with the lean mixture or cruising conditions in aircraft engines.

The other aviation-fuel test method, the rich-mixture or supercharge test, is known as the CRC-F-4-443 method. This method utilizes a standard single-cylinder CFR engine, which is connected to a dynamometer for measuring power output and is supplied with air under pressure that can be varied. The fuel and air supplied to the engine are measured and can be varied in mixture ratio over the full range in which ignition and combustion are possible within the combustion chamber. In the process of a test, the engine is operated on the test fuel under conditions of least audible knock of as nearly uniform intensity as possible throughout the range of fuel-air ratio from "full lean" to "full rich." The test is repeated with high and low reference fuels that rate either above or below the test sample.

The readings of fuel-air ratio of each test point, plotted as abscissa, against corresponding indicated mean effective pressure of those points, plotted as ordinates, establish a curve of mixture-response of the fuel. Direct interpolation between the curve of the test fuel and the upper and lower bracketing fuel establishes the rich rating of the test fuel.

The following discussion of the year's work on fuel testing in engines is conveniently considered according to the type of test used.

Fuel Response in Spark-Ignition Engines (Aviation and Motor)

Aviation fuels, lean-mixture test. - Three hundred twenty ratings were made by the CRC-F-3 aviation fuels lean-mixture test method. More than 170 of these ratings were made on small fractions from the pilot-plant superfractionation of two naphthas - one from the Oklahoma City field, Oklahoma (see footnotes 27 and 28), and the other from the Santa Barbara field in Venezuela, South America. Several ratings were made in the 115/145-grade aviation-fuel study on a condensate from the Lake Creek field, Texas.

The conventional indicator used on the F-3 test unit was superseded by a strip-chart temperature recorder. This instrument was a definite aid in interpreting engine results and in improving the precision of rating. Figure 16 shows the installation of this engine test unit with both temperature indicators mounted for use.

Aviation fuels, supercharge test. - One hundred ratings were made by the CRC-F-4 aviation-fuels supercharge method. Engine ratings were made on fractions and blends of the Oklahoma City naphtha and Lake Creek condensate to determine the quantity of 115/145-grade base stock that could be obtained by superfractionating these naphthas.

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An electronic detonation indicator was installed on the F-4 unit for use in rating fuels by the supercharge method. This instrument can be seen in the edge of the instrument panel desk in figure 17, which shows the supercharge engine installation.

Motor fuels. - One of the two F-3 test units was converted to an F-2 unit for rating fuels in the motor-gasoline range. One hundred ninety ratings have been made on this engine since November 1945. Approximately 150 of these tests were on fractions from the superfractionation of naphtha from the Santa Barbara field, Venezuela, South America.

An electronic strip-chart recorder was installed to supplement the instrumentation on the F-2 unit. This recorder is very useful in analyzing the results of ratings by different procedures and in interpreting the influence of engine variables. The complete installation, including recorder, is shown in figure 18.

Cooperative work. - As previously mentioned, all the methods use reference fuels that must be calibrated first. The engine laboratory was an active participant in the calibration of leaded blends of technical isooctane, toluene, and M-fuel which were proposed to the CFR committee as secondary reference fuels. Rating data were reported to the Coordinating Research Council. The laboratory also participated in the calibration of leaded blends of triptane and normal heptane by the lean- and rich-rating methods for the purpose of determining the suitability of these fuels as primary reference fuels for rating aviation fuels. The data on all of these reference fuels were submitted to the Coordinating Research Council. The results indicate the possibility of developing a fuel-rating scale that will supersede the present octane scale.

Rating of monthly samples of aviation gasoline distributed by the National Aviation Exchange Group was continued throughout the year, with the inclusion of ratings by the F-2 motor method in February 1945. The laboratory made a good showing in the rating of these samples during the calendar year 1945. The Bureau's laboratory was fourth among 34 laboratories in precision of rating by the F-3 method and third among 35 laboratories in precision of rating by the F-4 method.

Despite termination of the war, the local Tulsa-Bartlesville Regional Operation and Maintenance Group (a part of the Coordinating Research Council organization) has continued its activities but devoted its attention to motor fuels. The membership has increased from 13 to 25 laboratories, which reflects revived interest in motor fuels. Samples were rated monthly, and the data were submitted to the Bureau's representative, who, as leader of the group, prepared summary reports of their results. At quarterly meetings, engine-operating techniques and equipment-maintenance problems were discussed among engine operators representing member laboratories. The Bureau representative, as leader of the group, has conducted these meetings and prepared minutes of each meeting and distributed them to member laboratories, to leaders of other regional groups, and to interested members of the Coordinating Research Council.

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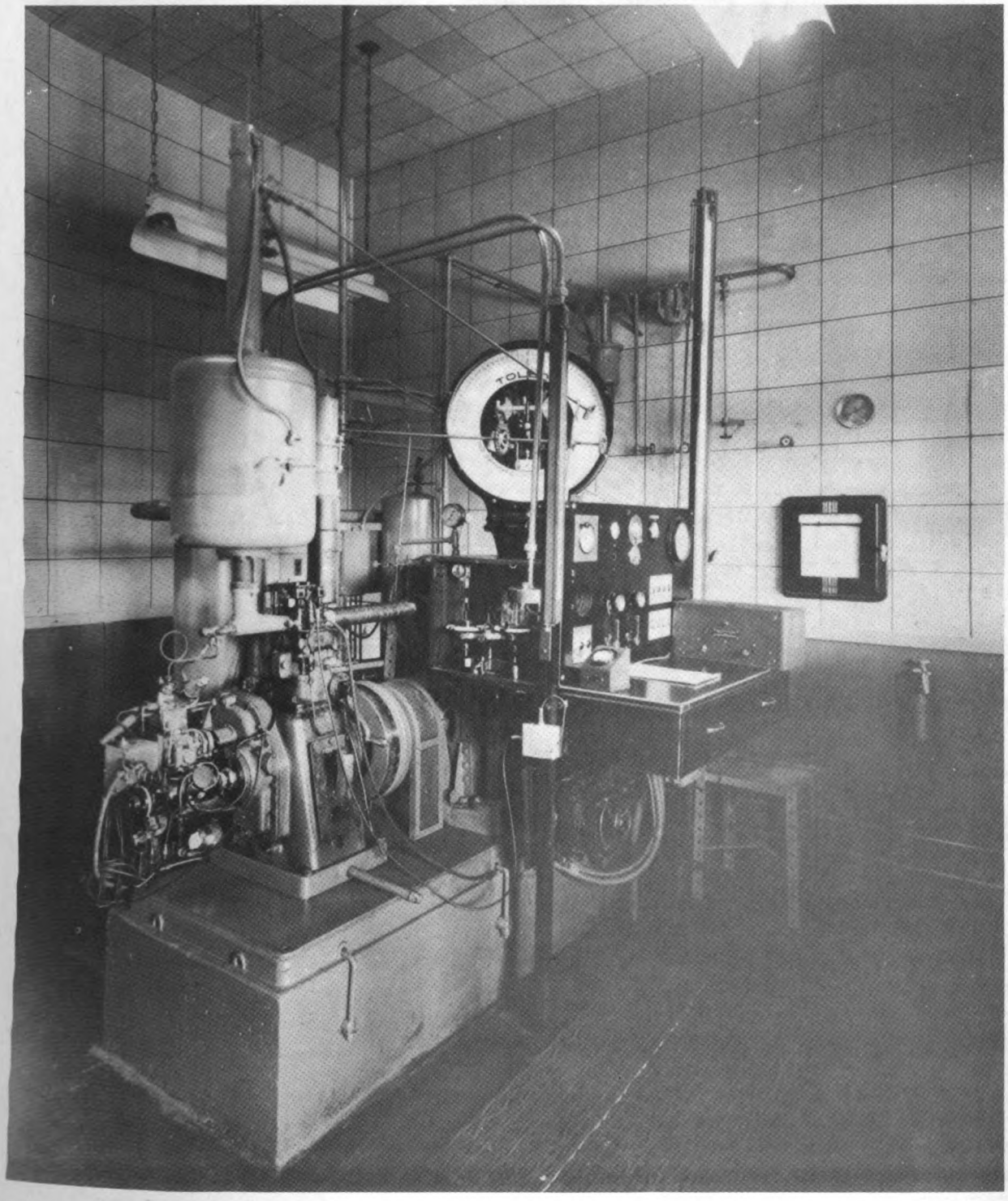

gure 17. - CFR supercharged fuel-research unit for determining knock characteristics of aviation fuels.

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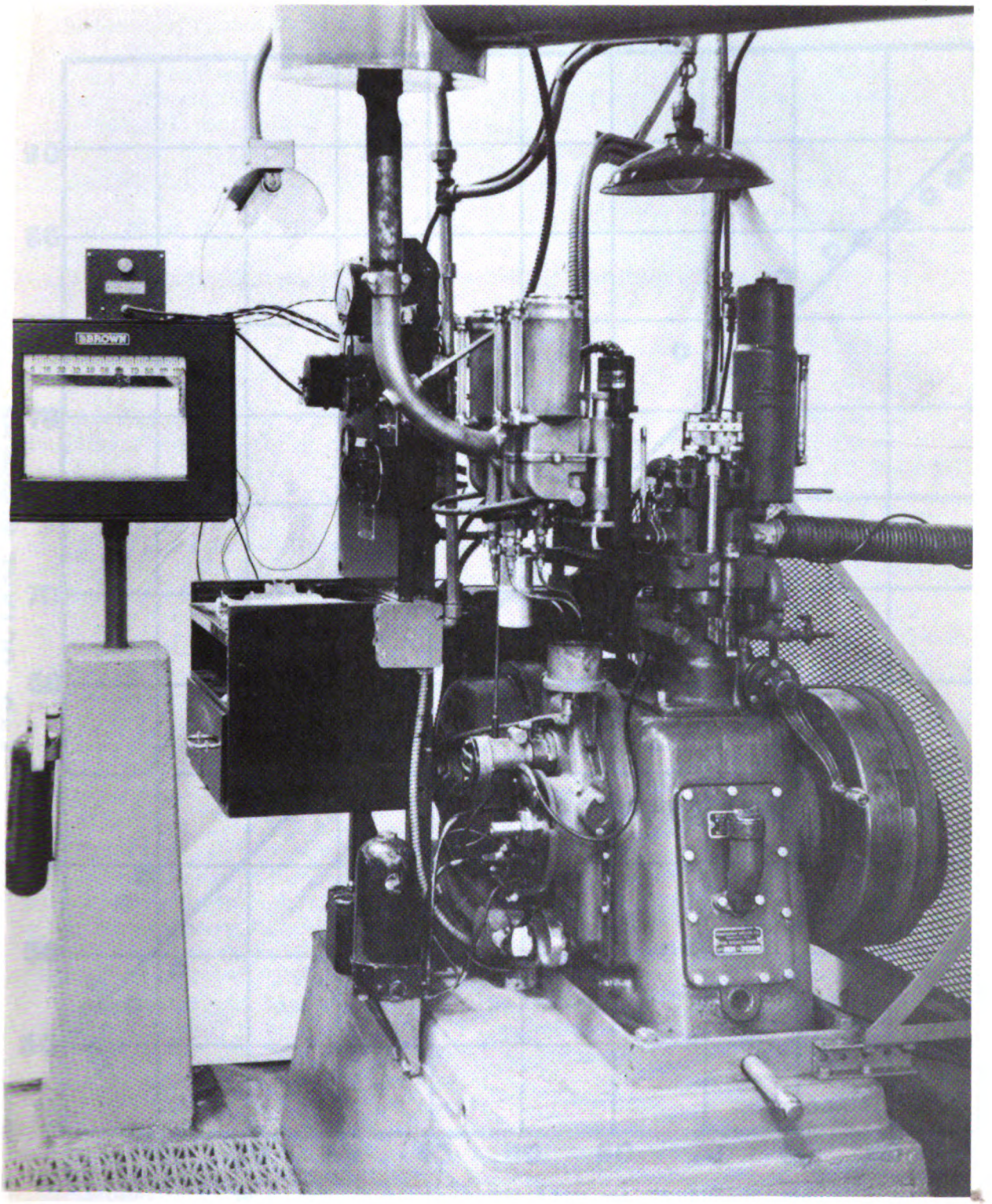

Figure 18. - ASTM-CFR fuel research unit for determining the knock characteristics of motor fuels.

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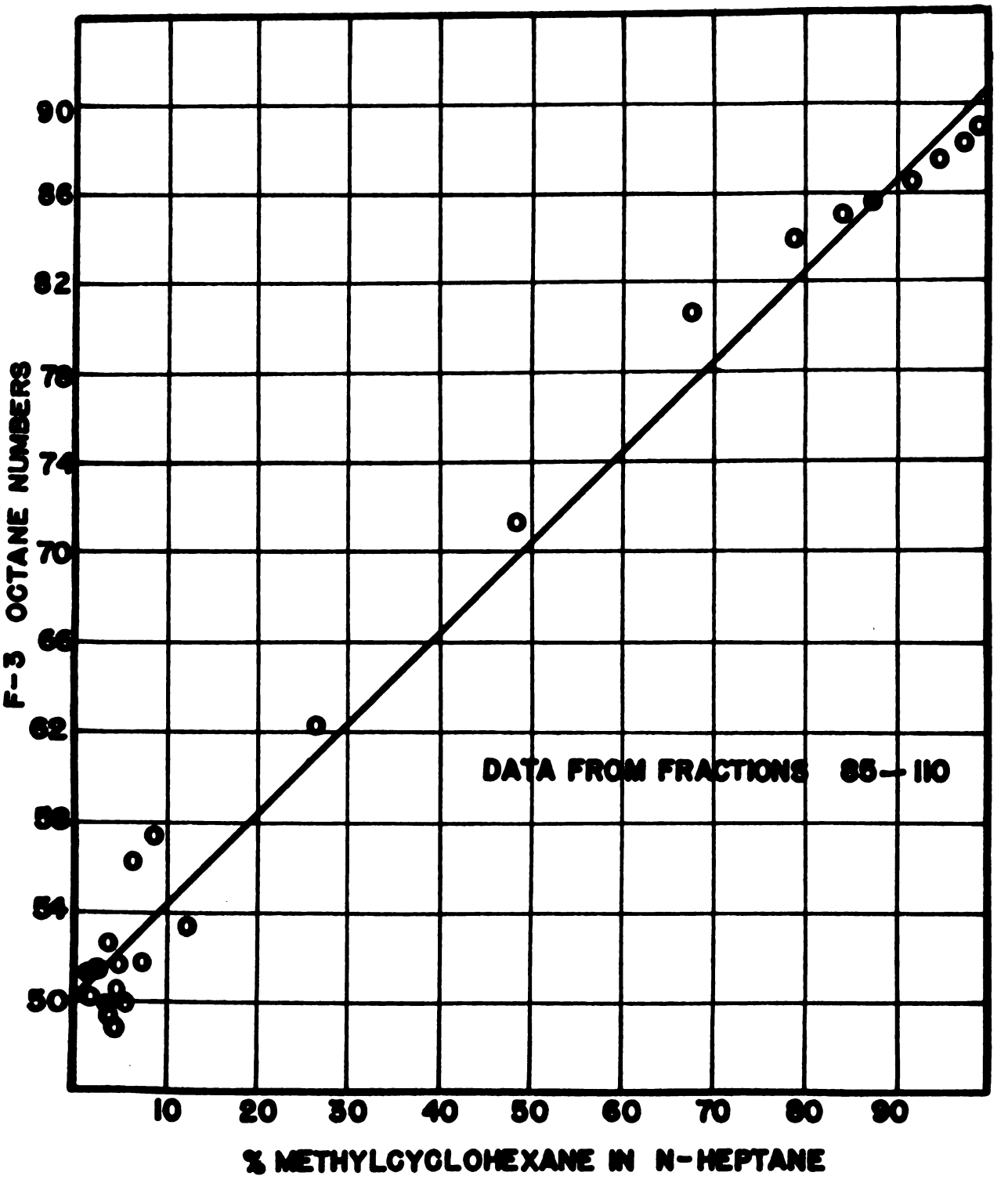

Figure 19. - Octane number of fractions containing methylcyclohexane in n-heptane.

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Rating data on the second lot of 10 samples of aviation fuel, rated by the local group, were analyzed, and the analysis 37/ was reported to member laboratories and the Coordinating Research Council. This report provided information on the precision in rating aviation fuels attained by the several participating laboratories.

Fuel Response (Diesel) in Compression-Ignition Engines

The parts for converting and F-2 or F-3 unit to a CRC-F-5 Diesel-fuel test unit were obtained. Published data on Diesel-fuel testing were reviewed to aid selection of equipment and procedures for testing such fuels.

Relationships of Engine Response, Fuel Composition and Fuel Properties (Physical and Chemical)

Testing fuels in engines is expensive and time-consuming and often cannot be done at all in experimental work because of insufficiency of material. Frequently, the need for such tests could be obviated if it were possible to calculate the octane number from the octane number of the components, which are often easily obtainable. The combined data of the superfractionation studies, analyses of the fractions therefrom, and engine test data on the fractions afforded a unique opportunity to obtain blending octane numbers of hydrocarbons.

Thus, the CRC-F-3 method octane-number blending values of 24 hydrocarbons at a tetraethyllead concentration of 4 ml. per gallon were calculated from the hydrocarbon-analysis and octane ratings of 130 fractions from the superfractionation of an Oklahoma City naphtha (footnote 28). Most of the fractions contained only two hydrocarbons in addition to benzene, toluene, or ethyl benzene whose F-3 octane ratings with 4 ml. TEL/gal. are fairly well-established as 97, 100, and 102, respectively. The values for these aromatics were accepted as accurate, and the octane numbers of the other two constituents were determined graphically, as shown in figure 19 for methylcyclohexane and n-heptane. The octane number that a blend of the nonaromatic components of a fraction would have if blended in the ratio in which they occur in the fraction was calculated, and the octane number so obtained was plotted against the percentage of methylcyclohexane in normal heptane. A straight line was drawn through these points, using the method of averages, and the 100-percent methylcyclohexane intercept was called the blending octane number of methylcyclohexane, whereas the zero-percent methylcyclohexane intercept was called the blending octane number of the n-heptane. The data points for this mixture defined a fairly good line, but with some other mixtures the two nonaromatic hydrocarbons occurred in only a few fractions and in approximately the same relative percentages, so that the slope of a line through the data points could not

37/ Tulsa-Bartlesville Regional Report #2 - Analysis of Engine Rating and Injection Data on Samples TB-11 through TB-20, compiled by C. R. Sponsler.

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be established definitely. Most of the hydrocarbons for which the data are doubtful, however, were present only in small percentages, and the errors are not large enough to affect appreciably octane numbers calculated for the isocuts or for naphthas. The blending octane numbers of the hydrocarbons in these naphthas, as calculated from the composition, and octane numbers of the fractions are listed in table 5. Table 6 illustrates the precision of calculated octane numbers, using the values from table 5, as compared with determined values of the several cuts and naphthas.

The apparatus used to prepare blends of fuels for engine testing was reconstructed to utilize nitrogen gas instead of water to displace the fuels from their containers and thus avoid contamination. This apparatus was used in preparing the blends required to select a base stock suitable for use in 115/145-grade aviation fuel by superfractionation of an Oklahoma City naphtha. From the engine data and composition of these blends, ternary diagrams were prepared to enable selection of the 115/145 grade fuel. This equipment was also used to prepare reference-fuel blends for the supercharge procedure. The blending laboratory also prepared 33 blends necessary for the engine calibration of leaded technical isooctane, M-reference fuel, toluene, and eleven blends of leaded triptane in n-heptane for calibration in both F-3 and F-4 engines.

TABLE 5. - Calculated F-3 blending values of hydrocarbons with 4.0 ml. tel

PARAFFINS

Hydrocarbon	Blending Octane No.
2,3-Dimethylbutane	106
2-Methylpentane	93
3-Methylpentane	97
n-Heptane	64
2,2- and 2,4-Dimethylpentane	97
2,3-Dimethylpentane 2-Methylhexane	89
3-Methylhexane	92
n-Heptane	50
Dimethylhexanes	80
2- and 4-Methylheptanes	71
3-Methylheptane	72
n-Octane	39

NAPHTHENES

Methylcyclopentane	97
Cyclohexane	86
trans-1,3-Dimethylcyclopentane	96
Methylcyclohexane	90
Ethylcyclopentane	89
Trimethylcyclopentanes	97
trans-1,3- and 1,4-Dimethylcyclohexanes	91
trans-1,2-Dimethylcyclohexane	91

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TABLE 5. - Calculated F-3 blending values of hydrocarbons with 4.0 ml. tel (Cont'd.)

AROMATICS

Hydrocarbon	Blending Octane No.
Benzene	97
Toluene	100
Ethylbenzene	102

TABLE 6. - Comparison of calculated and determined F-3 octane numbers (4.0 ml tel/gal.) of the individual cuts from three naphthas

Oklahoma City

Fraction	Calculated O.N.	Determined O.N.	Difference
Isohexane cut	100	100	0
Isoheptane cut	92	91	+ 1
Isooctane cut	90	88	+ 2
Iso C_6 + Iso C_7 blend	94	95	- 1
Iso C_6 + Iso C_7 + Iso C_8 blend	94	93	+ 1

East Texas

Iso C_6 cut	99	100	-1
Iso C_7 cut	94	91	+3
Iso C_8 cut	87	86	+1
Iso C_6 + Iso C_7 blend	94	95	-1
Iso C_6 + Iso C_7 + C_8 blend	91	91	0

Hull Silk Sikes

Iso C_6 cut	98	100	-2
Iso C_7 cut	93	93	0
Iso C_8 cut	88	86	+2
Iso C_6 + Iso C_7 blend	94	97	-3
Iso C_6 + Iso C_7 + Iso C_8 blend	91	92	-1

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Comparison of calculated and determined F-3 octane numbers (4.0 ml tel/gal.) of several naphthas, boiling range 97° to 243° F.

Naphtha	Calculated O.N.	Determined O.N.	Difference
Tom O'Conner	88	86	+2
Coalinga	89	89	0
Saxet	91	89	+2
Old Ocean	86	87	-1
K.M.A. Strawn	84	85	-1
Golden Meadow	88	88	0
Chapel Hill	82	83	-1
Conroe	89	89	0
Plymouth	89	90	-1
Segno	88	90	-2
Jennings	88	87	+1
Wade City	91	89	+2
Carthage	84	84	0

General Laboratory

Routine Examination of Crude Oils

During the year, Hempel analyses were made on 100 crude-oil samples. The crude oils analyzed were from new fields or formations and were distributed among the States as follows: Oklahoma, 20; Texas, 20; Mississippi, 18; New York, 7; California, 5; Pennsylvania, 4; Colorado, 14; Kansas, 2; Alabama, 1; Nevada, 2; Tennessee, 1; Wyoming, 1; Utah, 1; and 4 not identified. The samples from Nevada were oil seepages into water wells.

Definite action was initiated to procure the samples of foreign crude oil as well as of United States oil that are needed to provide current complete coverage of all important fields.

A report on Louisiana crude oils 38/ was completed for publication, and analyses of crude oils from two formations of the Rangely, Colo., field were released for publication 39/. Preparation of a report on the detailed procedure for making the Bureau of Mines crude-oil analysis was about 50 percent complete by the end of the year.

A paper 40/ discussing the relationships of crude-oil characteristics and stratigraphic occurrence was presented at the annual meeting of the American Association of Petroleum Geologists by one of the authors (N. W. Bass)

38/ Blade, O. C., and Garton, E. L., Properties of Louisiana Crude Oils. III. Additional Analyses: Bureau of Mines Rept. of Investigations 4034, 1947, 50 pp.

39/ Press release of March 6, 1946 (P.N.126792).

40/ Neumann, L. M., Bass, N. W., Giner, R. L., Mouney, S. F., Newman, T. F., Refniber, Charles, and Smith, H. M., Relationship of Crude Oil and Stratigraphy in parts of Oklahoma and Kansas.

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and will be published in the Bulletin of that organization. This paper is based upon interpretation of several hundred crude oil analyses, all made by the Bureau of Mines in cooperation with the Association.

Standard Inspection Tests of Petroleum Products

The diversity of this type of work in the general laboratory is shown by the following tabulation:

Test performed	No. of tests
Sulfur by "bomb" method	297
Sulfur by "lamp"	62
Bromine No.	277
Aniline point	209
Gasoline distillation	202
Hydrocarbon analysis	142
Specific gravity	156
Tetraethyllead content	140
Flask and fire points	39
Reid vapor pressure	84
Refractive index	47
Cloud point	20
Catalyst analysis	13
Group sulfur analysis	5
Miscellaneous	9
Total	1,718

A total of 7,283 determinations was made on these 1,718 samples. Virtually all of this work related to the various samples prepared by other groups in the course of their research.

Cooperative Work

Cooperative work with the American Society for Testing Materials was conducted, which involved:

1. Determination of aniline point (Subcommittee XVIII) of dark oils by an improved U-tube method and the Shell continuous-film apparatus.

2. Comparison of results obtained by volumetric and gravimetric methods for sulfur determination (Subcommittee VII) when analyzed by the lamp method.

3. Evaluation of lead content (section VII, Tech. Comm. A) of standard lead nitrate solution by the "chromate", "sulfate", and "molybdate" methods. These results, with other cooperative data, will enable the committee to determine the precision of the basic methods of analysis for tetraethyllead and to prepare a program for determining the best method for analysis of tetraethyllead in gasoline samples.

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Miscellaneous

National Motor-Gasoline Semiannual Survey

Surveys of motor gasoline have been made semiannually since 1936 in cooperation with the Coordinating Fuel Research Committee of the Coordinating Research Council, Inc., with the exception of 1942, when two of the reports were omitted. The usual surveys were made during the fiscal year 1946. The survey report for the summer of 1945 was released in January 1946,41/ whereas the compilations of data for the winter of 1945-46 were completed by June 1, and the report was released in July 1946 42/.

The second of these two surveys shows that motor gasolines had attained the highest quality of record in respect to octane ratings, whereas the report made 6 months earlier shows the average octane ratings were six octane numbers lower, reflecting wartime restrictions. The national average A.S.T.M. octane rating (motor method) of premium-price gasoline for the winter of 1945-46 was 80.9, and that for the summer of 1945 was 74.9. The octane number of regular-price gasoline for the winter of 1945-46 was 75.9, in contrast with 69.7 for the summer of 1945. These abrupt changes of 6.0 and 6.2 octane numbers due to ending of the war can be compared to gradual increases in octane numbers over a 5 1/2 -year period preceding the war, when octane ratings of premium and regular-price gasolines rose 3.7 and 5.2 octane numbers, respectively.

In addition to the octane values by the A.S.T.M. method, the report contains data on gravity, sulfur content, Reid vapor pressure, research octane number, and values from the distillation for regular and premium-price gasolines and for a few third-grade motor fuels. Study of the data of these other properties indicates a trend to lighter, more volatile gasolines.

Figures 20 and 21, from the surveys, show the trend in octane number, vapor pressure, and three distillation-temperature points for the two grades of gasoline during the winters and summers, respectively.

Also included in the reports for the last two surveys is a map of the United States that shows the distribution of the samples collected and tested by the cooperating companies. Figure 22 is such a map for the survey of winter 1945-46, which shows 237 locations in 21 districts. The number of samples from each location (a location may include several cities) is indicated graphically as well as by numerals. A total of 3,735 individual analyses, representing the products of 100 marketers of gasoline, were submitted by 19 petroleum-testing laboratories. These analyses are of samples collected in 318 cities in 44 States and the District of Columbia. The radial chart on figure 22 illustrates the distribution of samples among the districts. Inspection of the map reveals fair representation of samples within each district.

41/ Blade, O. C., National Motor-Gasoline Survey, Summer 1945: Bureau of Mines Report of Investigations 3883, 1946, 34 pp., 3 figs.

42/ Blade, O. C., and Sponsler, C. R., National Motor-Gasoline Survey, Winter 1945-46: Bureau of Mines Report of Investigations 3959, 1946, 39 pp. 3 figs.

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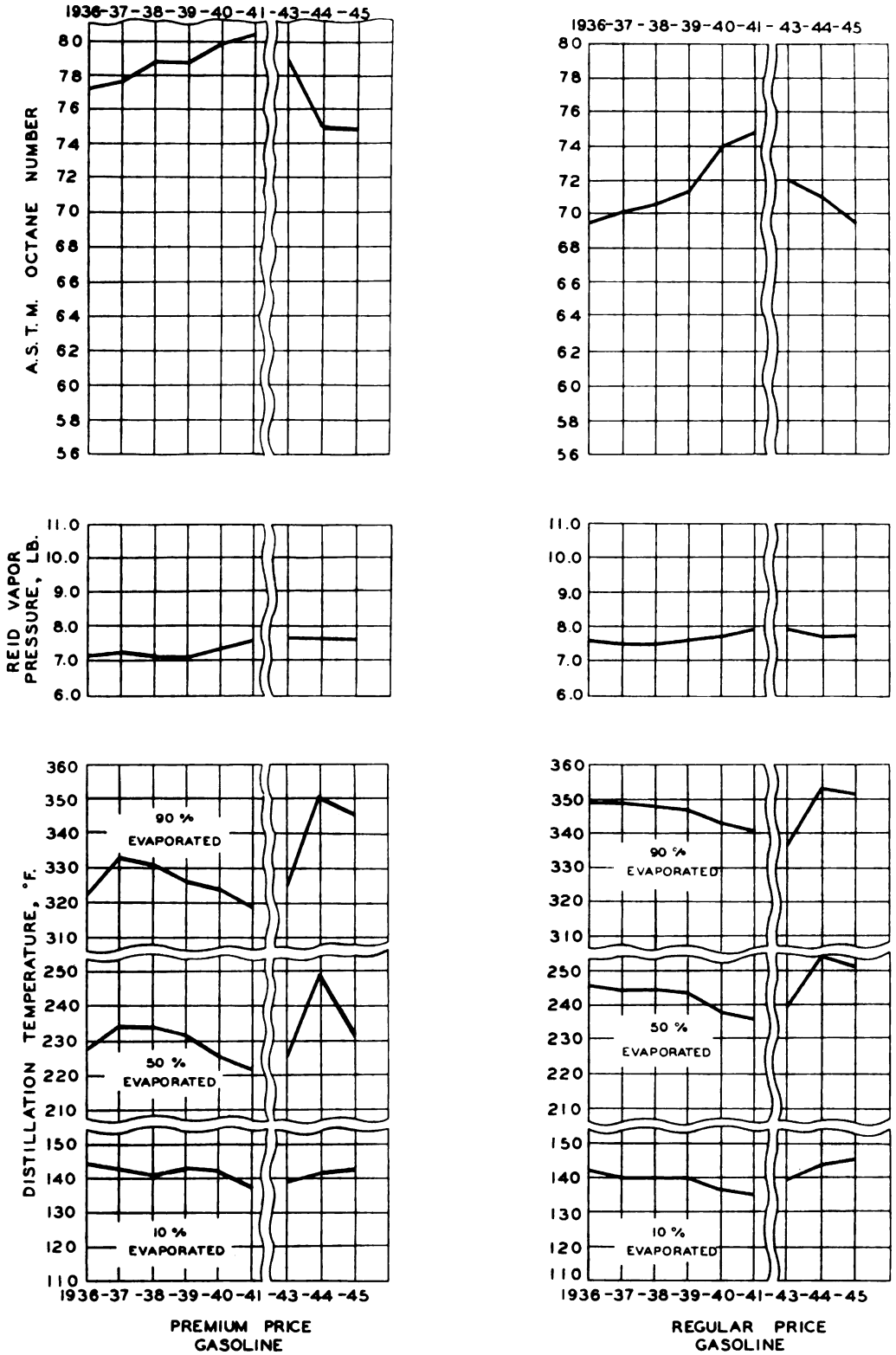

Figure 20. - Comparison of gasoline characteristics from summer surveys of 1936 through 1945.

No plots are shown for the summer of 1942 as the surveys were discontinued during 1942.

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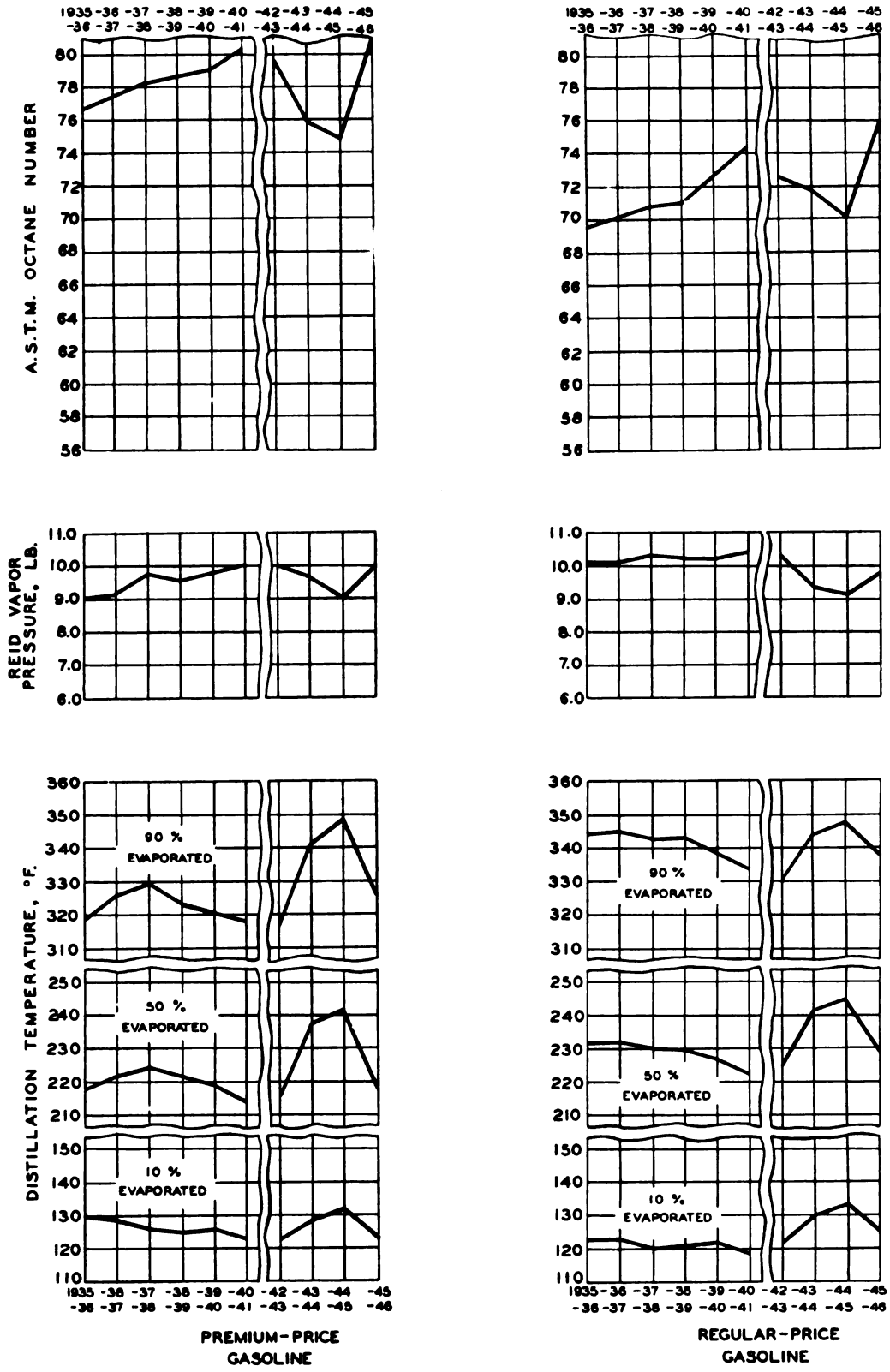
A.S.T.M. OCTANE NUMBER
REID VAPOR PRESSURE, LB.
DISTILLATION TEMPERATURE, °F.
90 % EVAPORATED
50 % EVAPORATED
10 % EVAPORATED
1935-36 -37 -38 -39 -40 -42-43 -44 -45
-36 -37 -38 -39 -40 -41 -43-44 -45 -46
PREMIUM-PRICE GASOLINE
REGULAR-PRICE GASOLINE

Figure 21. - Comparison of gasoline characteristics from winter surveys of 1935-36 through 1945-46.

No plots are shown for the winter of 1941-42 as the surveys were discontinued during 1942.

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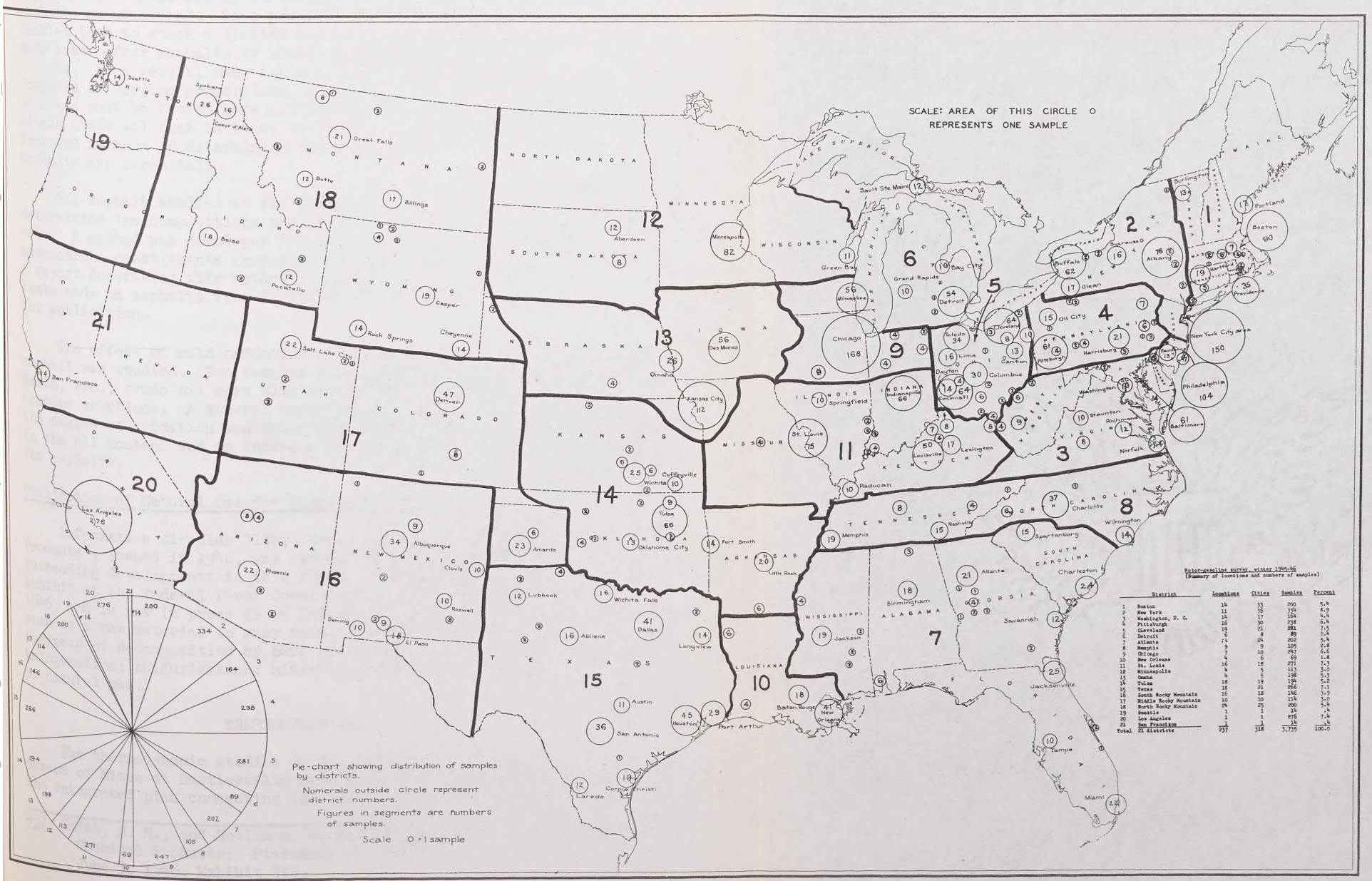
SCALE: AREA OF THIS CIRCLE O
REPRESENTS ONE SAMPLE
Pie-chart showing distribution of samples by districts.
Numerals outside circle represent district numbers.
Figures in segments are numbers of samples.
Scale O = 1 sample
Motor-gasoline survey, winter 1945-46
(Summary of locations and numbers of samples)
District | Locations | Cities | Samples | Percent
1 Boston 14 33 200 5.4
2 New York 11 36 334 8.9
3 Washington, D. C. 14 17 164 4.4
4 Pittsburgh 16 30 238 6.4
5 Cleveland 19 21 281 7.5
6 Detroit 6 6 89 2.4
7 Atlanta 14 24 202 5.4
8 Memphis 9 9 105 2.8
9 Chicago 7 10 247 6.6
10 New Orleans 4 8 69 1.8
11 St. Louis 16 16 271 7.3
12 Minneapolis 4 4 113 3.0
13 Omaha 4 4 198 5.3
14 Tulsa 18 19 194 5.2
15 Texas 16 21 266 7.1
16 South Rocky Mountain 16 16 146 3.9
17 Middle Rocky Mountain 10 10 114 3.0
18 North Rocky Mountain 24 25 200 5.4
19 Seattle 1 1 14 .4
20 Los Angeles 1 1 276 7.4
21 San Francisco 1 1 14 .4
Total 21 districts 237 318 3,735 100.0

Figure 22. - Map showing locations and numbers of samples for the national motor-gasoline survey, winter 1945-1946.

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Asphalts from Wyoming Black Oils

During the war, the refining, storing, and marketing of petroleum asphalts was simplified by curtailing the number of types and grades of asphalts manufactured. This practice was favored by many refiners, as it enabled them to stock a limited number of hard asphalts that could be made into softer asphalts by blending with available gas oils from other sources. As a result, many asphalts, particularly paving asphalts, are composed of varying proportions of materials derived from different crude oils and must be tested more critically than asphalts prepared from a single crude oil that is known to yield satisfactory products. Accordingly, improved methods of determining the compositons and serviceabilities of asphalts are essential.

The asphalt studies at the Laramie station were directed toward determining the compositions and properties of asphalts from various crude oils. A method was developed for separating asphalts into three groups of hydrocarbon constituents commonly known as asphaltenes, resins, and oils. A report describing this method of analysis and the results of laboratory tests made on asphalts from 27 different crude oils is now being prepared for publication.

The effect of mild oxidation upon the compositions and properties of asphalt was studied. Two samples of a commercial asphalt from Oregon Basin, Wyo., crude oil were slightly oxidized by passing air through their benzene solutions. A general hardening of the asphalts in proportion to the degree of oxidation was observed. Oxidation also caused a decrease in the oil content and an increase in the resin and asphaltene contents of the asphalts.

Utilization of Natural Gas for Chemical Products

Information Circular 7108, "Utilization of Natural Gas for Chemical Products", issued in 1940, was extensively revised to include the many succeeding developments in this field. The report[43/] was presented as an exhibit at the Federal Power Commission hearings in Washington, July 17, 1946, and is now in press as an Information Circular. Natural gas can be used as a raw material in many chemical reactions, and the report covers the subjects of decomposition by heat, catalysts, and electric arc; oxidation; halogenation; sulfurization; nitration; and use of nonhydrocarbon components of natural gas.

THERMODYNAMICS OF PETROLEUM

The thermodynamic studies of the Petroleum Experiment Station of the Bureau of Mines at Bartlesville have been in active progress since May 1943. The integrated plan connecting the specific projects is to obtain all of the

43/ Smith, H. M., and Holliman, W. C., Utilization of Natural Gas for Chemical Products: Statement for Federal Power Commission, prepared June 3, 1946, Exhibit 312.

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data required to evaluate the free-energy equation for organic compounds over a wide range of temperature and pressure. This equation may be evaluated from purely thermal quantities or from other data by the methods of statistical mechanics, and the work in this laboratory has stressed the determination of quantities for the former method. The free-energy function is of considerable practical importance, because it allows the engineer to predict in advance the optimum conditions for maximum yields in chemical processes; also, it tells him if a proposed process will work at all. These data are of immediate practical importance to the petroleum industry, which is becoming more and more interested in utilizing petroleum as a raw material for the production of pure hydrocarbons and derivatives. In addition, as the data are fundamental in nature, they bear on many problems of theoretical interest to the organic and physical chemist. Because of this fundamental nature of the data, great stress has been placed on the final accuracy of the experimental results.

Engineers and chemists who are interested in practical manufacturing processes need these data in designing and operating plants economically and efficiently.

During the past year, work was continued on the general problems discussed on the following pages.

Heats of Combustion

Considerable work was done in order to obtain a satisfactory value for the heat of combustion of tetraethyllead. This substance is widely used as an antiknock fluid in internal-combustion motors, and a reliable value of its heat of formation is of great importance.

The experimental determination of this quantity is beset with difficulty because of the physical properties of the substance and because of the reactivity of the products of combustion. The lead in the compound is oxidized and when hot is extremely reactive. A great deal of effort was made to find a satisfactory method of eliminating the corrosive action of the products of combustion and of determining the amount of the reaction. The experimental results were never satisfactory, but a preliminary value was obtained and reported at the Atlantic City meeting of the American Chemical Society 44/. This particular problem has been discontinued for the present.

Some attention was given to the problem of measuring heats of combustion of halogen-containing compounds. This problem also offers many technical difficulties because of the chemical activity of the combustion products, but satisfactory progress has been made on it.

44/ Knowlton, John W., and Huffman, Hugh M., The Heat of Combustion of Tetraethyl Lead: Presented before American Chemical Society Atlantic City meeting, April 8-12, 1946. (Not published.)

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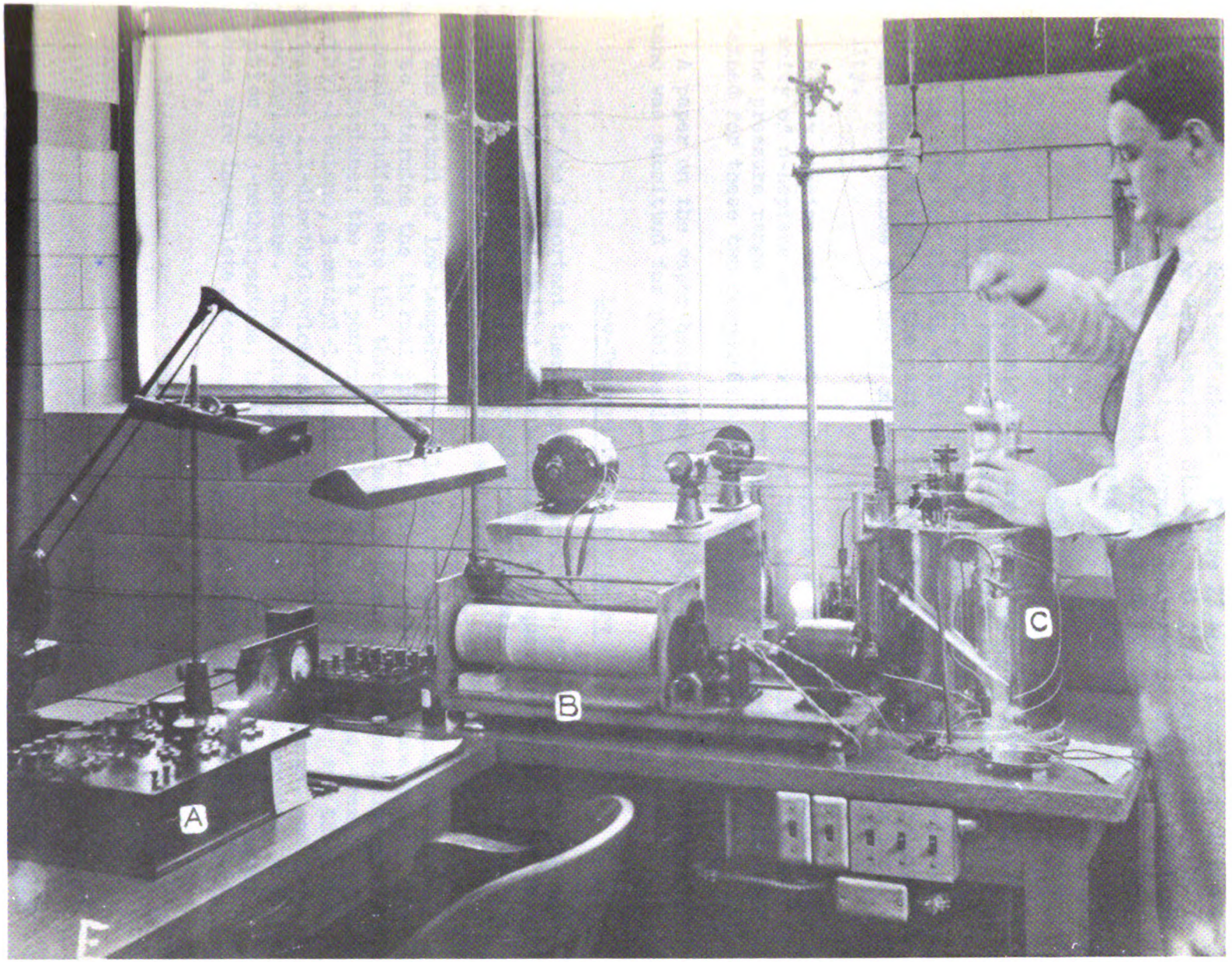

Figure 23. - Equipment for heats of combustion: A, Mueller bridge; B, chronograph; C, calorimeter assembly.

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The precise measurement of heats of combustion requires specialized equipment and highly developed skills. Figure 23 shows a portion of the equipment in use at the Bartlesville Station. At the extreme left is a Mueller-thermometer bridge used to determine temperature changes with high accuracy. In the center is shown the chronograph for recording the time of various events. The calorimeter assembly is shown at the right.

Flow Calorimetry

In order that thermodynamic data may have their greatest utility, it is necessary that they be known for solids, liquids, and gases over a range of temperature and pressure. An important thermodynamic quantity in connecting data for liquids with those for gases is the heat of vaporization. Experiments were made in the past year that showed that the flow calorimeter gave accurate values for heats of vaporization, thereby increasing its utility.

Highly precise and accurate measurements were made of the vapor heat capacity of n-heptane and n-hexane over the temperature range 50° to 200° C. and the pressure range 1/4 atm. to 1 atm. Heats of vaporization also were obtained for these two compounds and for benzene.

A paper on the vapor-heat capacity of n-heptane and 2,3,3,-trimethyl butane was submitted for publication 45/.

Low-Temperature Calorimetry

One of the important thermodynamic quantities is entropy, and the most practical and general method of determining this quantity is study of the thermal properties of a pure compound from extremely low temperatures, about 12° K., up to room temperature and higher.

The method of low-temperature calorimetry was used during the past year to determine the thermal properties of 12 additional substances. The compounds studied were the three hexanes - n-hexane, 2,2-dimethylbutane, and 3-methylpentane; the six pentenes - 1-pentene, cis-2-pentene, trans-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene; and the three naphthenes - 1,1-dimethylcyclohexane, cis-1,2-dimethylcyclohexane, and trans-1,2-dimethylcyclohexane. The entropies of all of the above compounds, with the exception of 3-methylpentane, have been calculated. The data on 3-methylpentane were incomplete, because it was not possible to crystallize this material.

45/ Waddington, Guy, Todd, Samuel S., and Huffman, Hugh M., Experimental Determination of the Vapor Heating Capacity of n-Heptane and 2,2,3-Trimethyl Butane: Presented before American Chem. Soc. Atlantic City Meeting, April 8-12, 1946.

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One paper reporting work done in low-temperature calorimetry was published,46/ and a second paper47/ has been accepted for publication.

The obtainment of highly precise and accurate thermodynamic data is a laborious and painstaking task requiring highly skilled and intelligent personnel and very specialized and precise equipment and instruments. To illustrate the type of equipment required in the measurement of heat capacities, a view of part of the specific heat laboratory is shown in figure 24. The bench in the foreground shows part of the assembly for the determination of vapor-heat capacities. The bench in the background shows the cryostat and vacuum system used in the low-temperature heat-capacity measurements. The complex electrical systems for both types of measurements are not shown.

46/ Douslin, Donald R., and Huffman, Hugh M., Heat Capacities, Heats of Transition, Heats of Fusion, and Entropies of Cyclopentane and Methylcyclohexane: Jour., Am. Chem. Soc., vol. 68, 1946, p. 173.

47/ Douslin, Donald R., and Huffman, Hugh M., Low-temperature Heat Capacities of the Five Isomeric Hexanes: Jour., Am., Chem. Soc., vol. 68, 1946.

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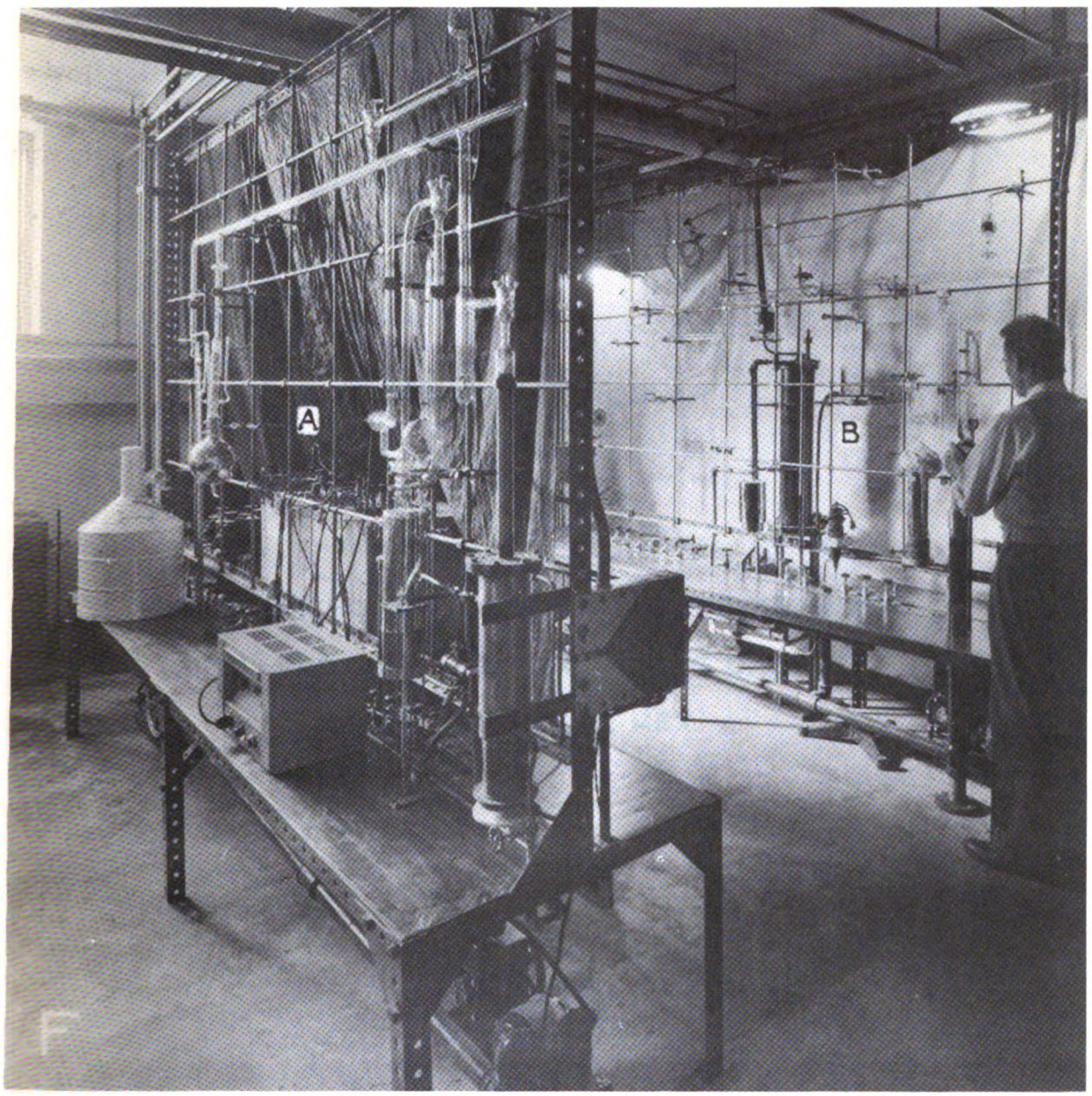

Figure 24. - Heat capacity laboratory. A, Assembly for flow calorimetry; B, crysotat and vacuum system for low-temperature calorimetry.

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